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APPROACHES TO LADDER STRUCTURES

V. THERMAL DECOMPOSITION AND POLYMERIZATION OF [2H], 3, 1-BENZOXAZINE-2, 4, [1H]-DIONE AND SOME OF ITS DERIVATIVES

GERARD A. LOUGHRAN

TECHNICAL REPORT AFML-TR-70-152

OCTOBER 1970

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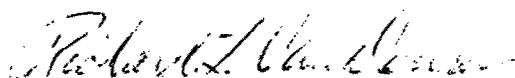
FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," and Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. G. A. Loughran as Project Scientist.

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This technical report has been reviewed and is approved.



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ABSTRACT

A new compound [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone was prepared by reaction of phosgene with 2,5-diaminoterephthalic acid.

The thermal decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione was studied as a model reaction. The reaction involves initial loss of carbon dioxide at 360°C and the formation of trimeric and tetrameric cyclic aryl amides, followed by dehydration to highly condensed structures.

[2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9[1H,6H] tetraone and 6,6'-bis-[2H],3,1-benzoxazine-2,4,[1H]-dione each were decomposed thermally under similar conditions. The resulting products were highly condensed cross-linked polymers of high thermal stability.

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SECTION I

INTRODUCTION

The existence of compounds containing a seven or eight membered ring system in which three or four atoms are suitably arranged to join two orthodisubstituted benzene rings together is illustrated by the molecules [5H]-dibenzo-[b,e][1,4]-diazepin-6-one (i.e., 5-dibenzodiazepinone), V, and dibenzo-[b,f][1,5]-diazocine-6,12,[5H,11H]-dione (i.e., diathranilide), XIV, respectively. Compound V has been conveniently prepared, starting with anthranilic acid, I, by reaction with o-chloronitrobenzene, II, at 200°C, in the presence of potassium carbonate and copper powder, to give 2-nitrodiphenylamine-6'-carboxylic acid, III. This was reduced in excess ammonium hydroxide with ferrous sulfate, to 2-aminodiphenylamine-6'-carboxylic acid, IV, which dehydrates in refluxing xylene to V (Reference 1). These reactions are illustrated in Figure 1. Dibenzo-[b,f][1,5]-diazocine-6,12,[5H,11H]-dione (dianthranilide), XIV, has been prepared by a number of methods. Schroeter first prepared XIV starting from anthranilic acid, I, which he converted to N-benzenesulfonylanthranilic acid, VI. This compound was readily converted to N-benzenesulfonylanthranoyl chloride, VIII, by reaction with PCL₅ in refluxing benzene. Dimerization of VIII to 5,11-bis-benzenesulfonyl-dibenzo-[b,f][1,5]-diazocine-6,12-dione, IX, occurred readily on treatment with pyridine (Reference 2). Compound IX gave dibenzo-[b,f],[1,5]-diazocine-6,12,[5H,11H]-dione, XIV, on treatment with fuming sulfuric acid, but 2-(o-aminophenyl)-3,1-benzoxazine-4-one, X, was formed when concentrated sulfuric acid was employed (Reference 3). Methyl anthranilate, XI, when treated with sodium in the presence of excess benzonitrile, gave a good yield of XIV

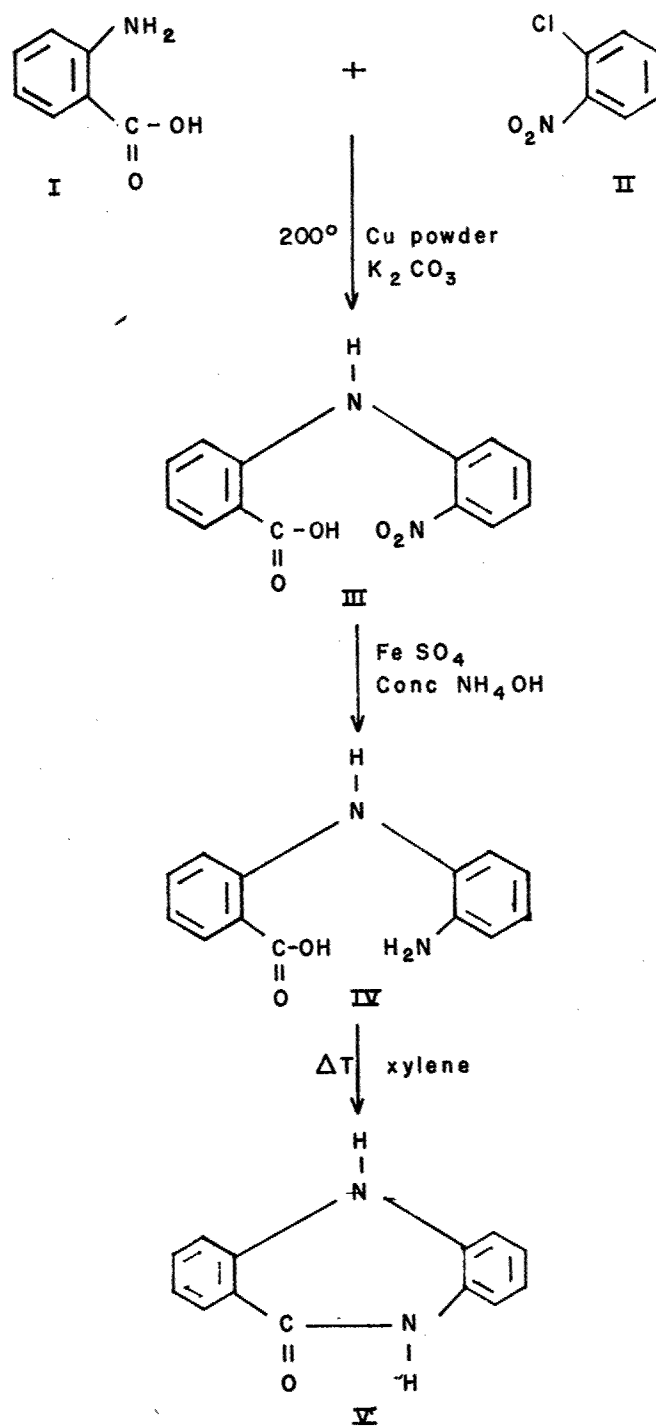


Figure 1. Preparation of 5-dibenzodiazepinone ([5H]-dibenzo-[b,e][1,4]-diazepin-6-one), V

along with a small amount of 2-phenyl-3,1-benzoxazine-4-one, XIII (Reference 4), which was also obtained by treatment of anthranilic acid with benzoyl chloride. The resulting product, N-benzoylanthranilic acid, VII, was converted to XIII by reaction with SOCl_2 (Reference 3). Compound XIV was also produced by the reaction of methyl anthranilate, XI, with acetonitrile or benzonitrile in the presence of sodium, and by the Beckman rearrangement of anthraquinone dioxime, XII, in polyphosphoric acid (Reference 4). The reactions are depicted in Figure 2.

Recently, Kurihara and Yoda reported the results of their investigation of the polycondensation of certain aromatic diaminodicarboxylic acids in polyphosphoric acid (References 5, 6, and 7). When benzidine-3,3'-dicarboxylic acid, XXVIII, was heated at 150°C in polyphosphoric acid in the presence of benzidine, a polymer having an inherent viscosity of 1.13 was obtained. In their papers (References 5 and 6) the polymer was characterized as a single-strand polyamide-amino acid, $\text{C}_{16}\text{H}_{12}\text{O}_6\text{N}_4$, XXX. However, in their patent (Reference 7), they claim that this polymer possesses a ladder-type structure containing dibenzo-[b,f][1,5]-diazocine-6,12,[1H,11H]-dione units and known as poly-(5,6,11,12-tetrahydro-6,12-dioxodibenzo-[b,f][1,2,5]-diazocine-2,8-diyl), XXXI. However, a repetition of this reaction under their conditions and an analysis of their experimental data (Reference 8) suggests that only a single-strand aromatic polyamide, $\text{C}_{16}\text{H}_{12}\text{O}_6\text{N}_4$, XXX, with pendant amino and carboxylic acid groups was obtained. Similarly, a polyamide amino acid, XXVII, from 2,5-diaminoterephthalic acid, XXV, was prepared. The reactions are illustrated in Figure 3.

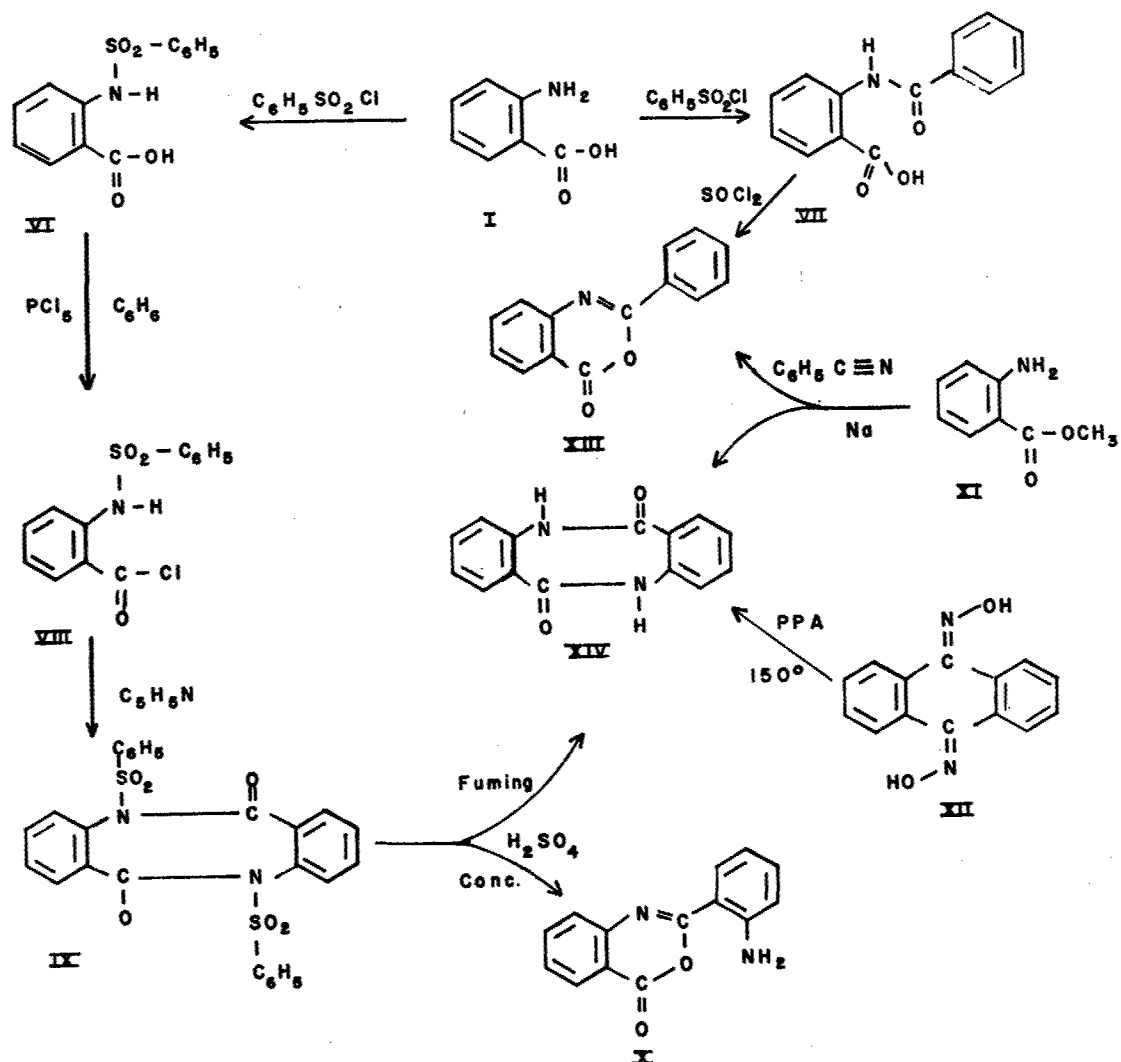


Figure 2. Preparation of Dibenzo-[b,f],[1,5]-diazocine-6,12,[5H,11H]-dione, XIV

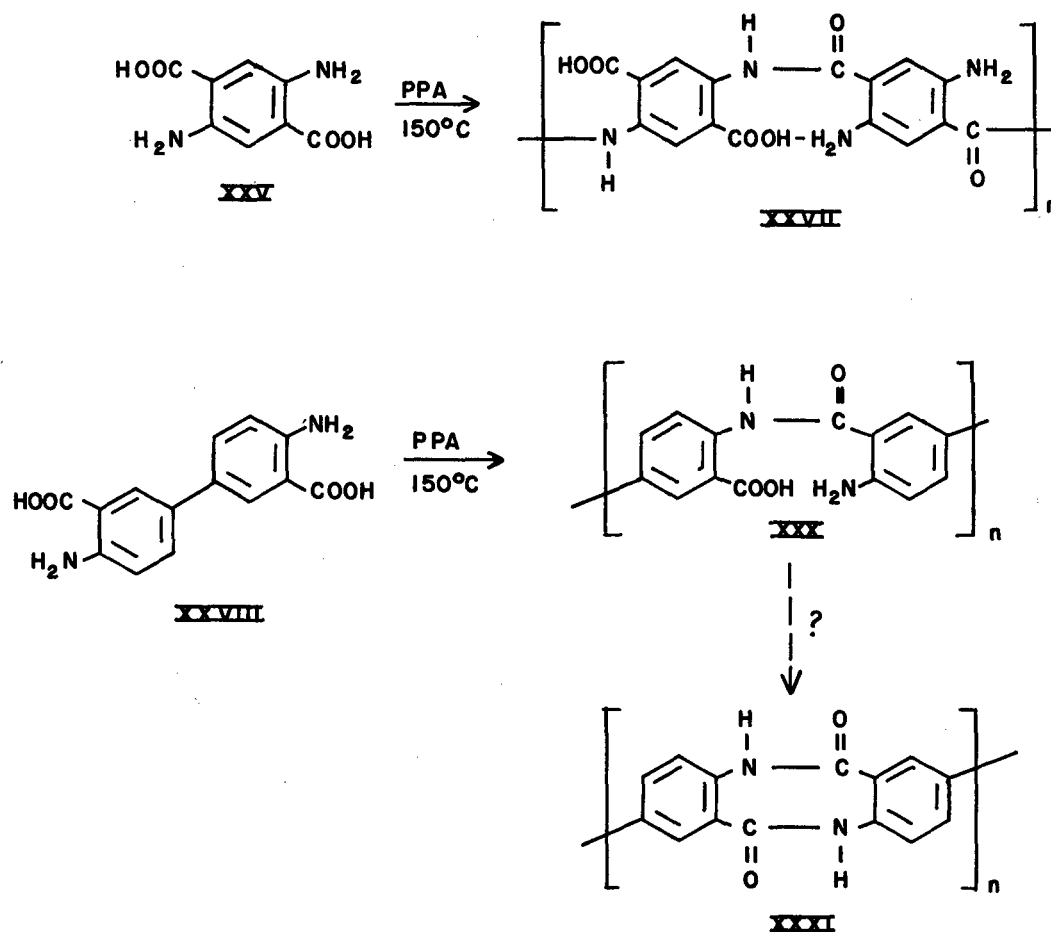


Figure 3. Condensation of Aryldiaminodicarboxylic Acids in Polyphosphoric Acid According to Kurihara and Yoda

The purpose of this work is to investigate the possibility of preparing ladder-type structures related to dibenzo-[b,f][1,5]-diazocine-6-12,[1H,11H]-dione, XIV, by the thermal decomposition of certain bis derivatives related to [2H],3,1-benzoxazine-2,4,[1H]-dione, XV. It became of interest to study the thermal decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV, as a model compound, and [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI, and 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX, as possible monomers for polymerization.

In regard to the thermal decomposition of the model compound, [2H],3,1-benzoxazine-2,4,[1H]-dione, XV, one might expect the initial loss of carbon dioxide (perhaps accompanied by or followed by loss of carbon monoxide), leading to the formation of free radicals such as A, if only loss of carbon dioxide is involved, and/or B, if loss of carbon monoxide is also involved. Recombination of the radicals can be expected to result in the formation of model compounds such as dibenzo-[b,f][1,5]-diazocine-6,12,[5H,11H]-dione, XIV, [5H]-dibenzo-[b,e][1,4]-diazepin-6-one, V, or dihydrophenazine, XXIII, or cyclic or linear polymers varying from the aromatic polyamide structure, XVI, XVIII, and XXI, to the mixed polyamideamine structure, XXII, or polyarylamine, XXIV. Such a possible reaction scheme is illustrated in Figure 4.

Similarly, the thermal decomposition of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI, might lead to the production of three possible radicals, A', B', and C', recombination of which could lead to a variety of possible structures, such as XXXI-XXXIV. Such a

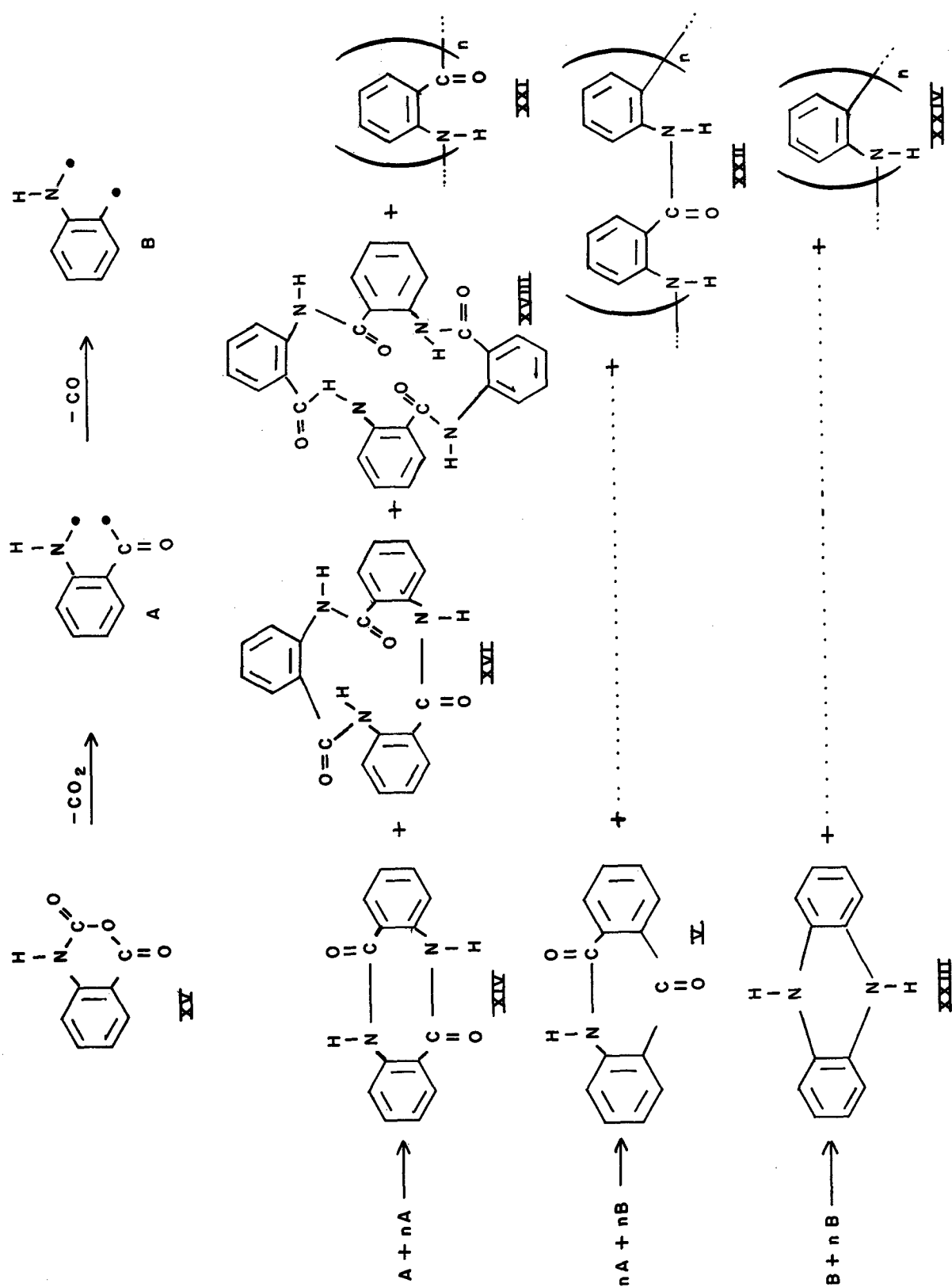


Figure 4. Scheme for Thermal Decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV

reaction scheme is depicted in Figure 5. Obviously 6,6'-bis-([2H],3,1-benzoxazine-2,4[1H]-dione), XXIX, should decompose in a like manner to give structures XXXV-XXXVIII. Its possible reaction scheme is illustrated in Figure 6.

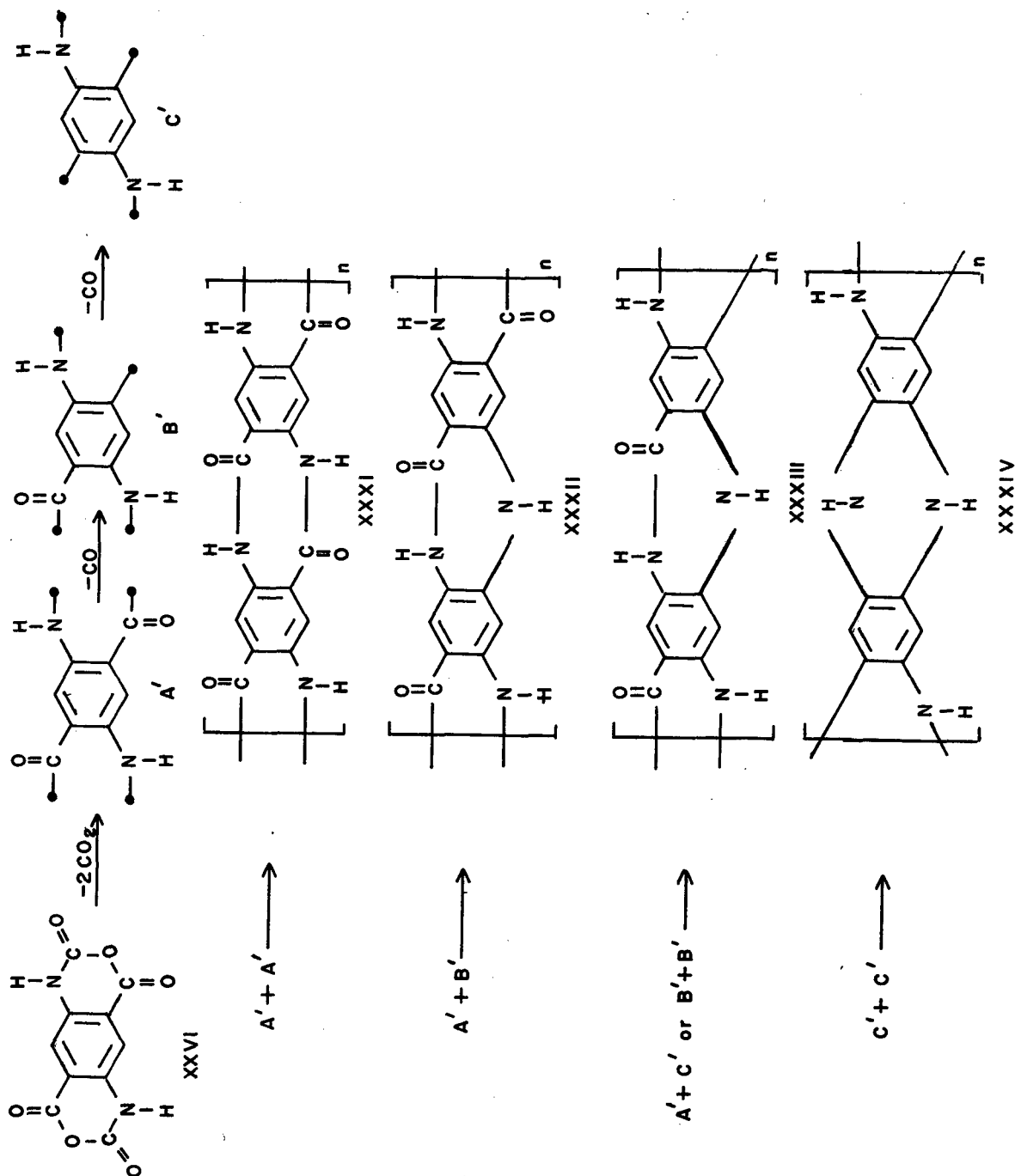


Figure 5. Scheme for Thermal Decomposition of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9, [1H,6H]-tetraone, XXVI

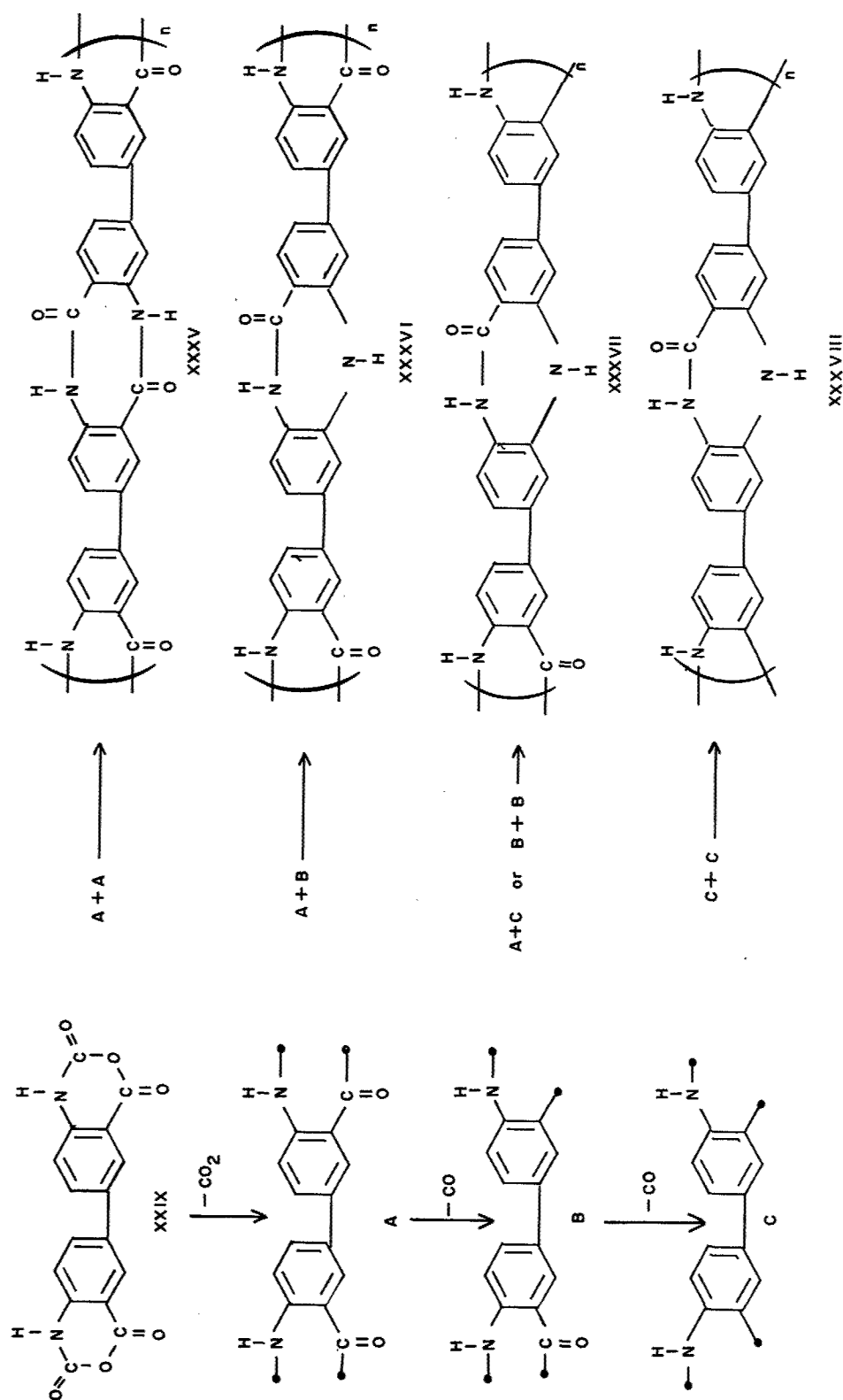


Figure 6. Scheme for Thermal Decomposition of 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX

SECTION II

DISCUSSION OF RESULTS

1. Preparation of Model Compounds and Monomers

The model compound, [2H],3,1-benzoxazine-2,4,[1H]-dione (isatoic-anhydride), XV, was prepared by the reaction of phosgene with anthranilic acid in dilute hydrochloric acid (References 9 and 10). Its infrared spectrum is shown in Figure 11.

A new monomer, [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI, not previously reported, was prepared similarly by reaction of phosgene with 2,5-diaminoterephthalic acid. It is a light-yellow granular solid which appears to decompose without melting near 330°C. Its infrared spectrum is shown in Figure 13. Its softening point curve (Figure 14) exhibits a sharp dip near 400°C. This is probably due to decomposition rather than to melting.

Another monomer, 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX, was prepared by reaction of benzidine-3,3'-dicarboxylic acid, XXVIII, with phosgene in hydrochloric acid (Reference 15). The compound apparently decomposes without melting above 360°C. Its softening point curve (Figure 16) shows a sharp dip near 425°C, which is most likely due to decomposition rather than to melting. The small inflection in the curve near 350°C, which might be interpreted as being due to softening or melting, might be caused by collapse after expansion of the packed solid particles on heating, or by release of trapped gases in the sample. Its infrared curve is exhibited in Figure 15. The infrared spectra of

[2H],3,1-benzoxazine-2,4,[1H]-dione, XV, [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI, and 6,6-bis([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX, have certain common features (Figures 12, 13, and 15). In all the spectra, a strong doublet appears at 1770 cm^{-1} and 1739 cm^{-1} . These bands are due to the carbonyl groups in 2 and 4 positions, respectively, on the oxazine ring (Réference 17). The bands appearing near 1010 cm^{-1} and 1040 cm^{-1} , near 1266 cm^{-1} , and in the $1300\text{--}1350\text{ cm}^{-1}$ may possibly be due to -C-O- stretching vibrations. The reactions involved in the preparation of XV, XXVI, and XXIX are illustrated in Figure 7.

2. Thermal Polymerization Reactions

The thermal decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV, was studied as a model reaction in order to obtain information on which free radicals are likely to be produced and what the predominant mode of radical recombination (Figure 4) might be. The compound was heated in a tube at 360°C under nitrogen for 21 days. Apparently a mixture of products resulted. The yellow material, 1-A, which sublimed on the walls of the tube was obtained in small quantity. Most of it appeared to dissolve in methanol. A small amount of a granular product, 1-A1, was obtained from this solution after cooling and standing. It appeared to have an empirical formula closely approximating $\text{C}_{21}\text{H}_{13}\text{O}_2\text{N}_3$, which may indicate a structure such as XVII. Its infrared spectrum (Figure 20) exhibited a single band near 1680 cm^{-1} which might be attributed to amide I carbonyl absorption. This infrared spectrum was not identical to those from either [5H]-dibenzo-[b,e][1,4]-diazepin-6-one, V, (Figure 18), or dibenzo-[b,f][1,5]-diazocine-6,12,[5H,11H]-dione, XIV (Figure 19).

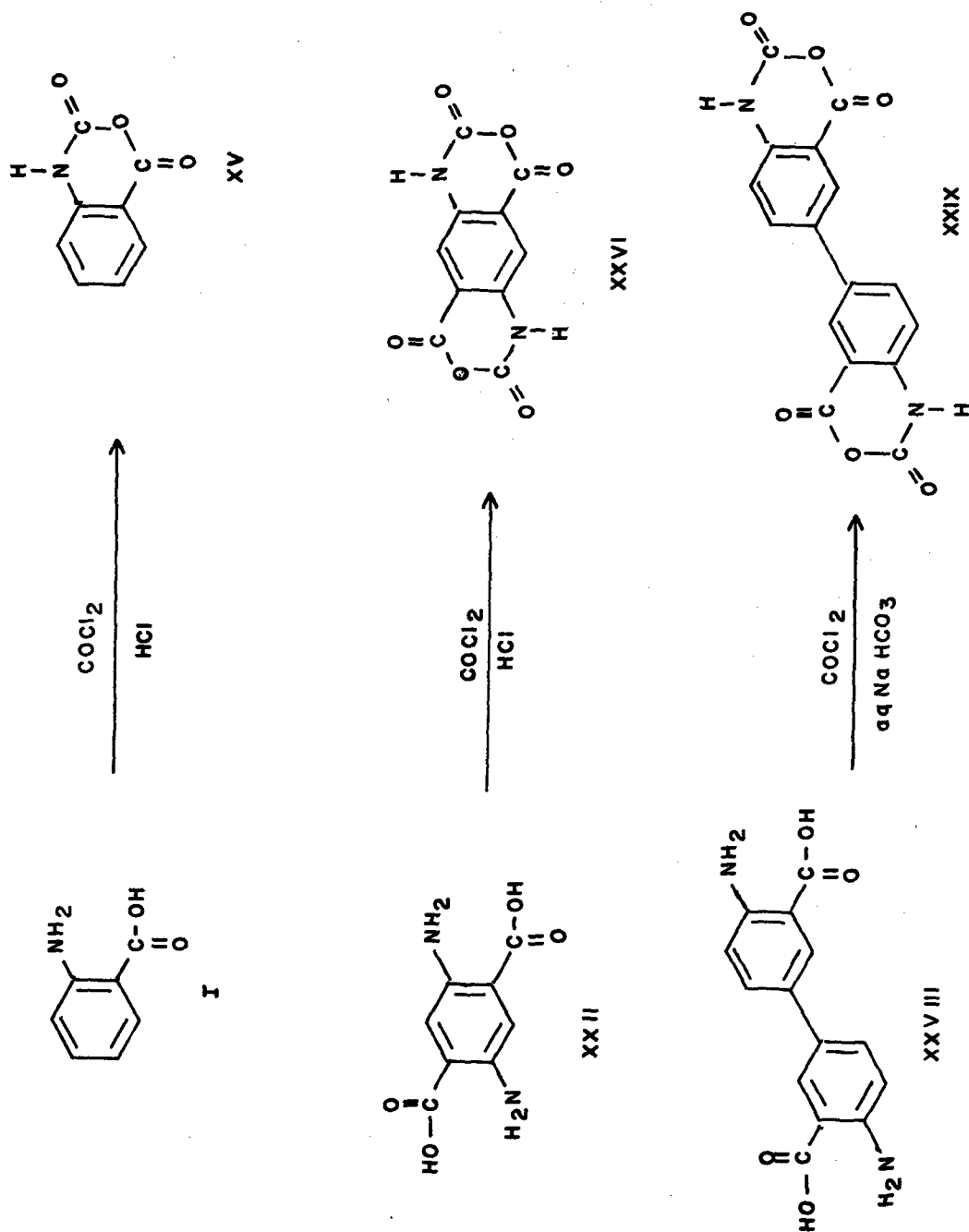


Figure 7. Preparation of [2H], 3,1-benzoxazine-2,4,6-trione, XV, [2H,7H], 3,1,8,6-benzobisoxazine-2,4,7,9,9,6H]-tetraone, XXVI, and 6,6'-bis-([2H], 3,1-benzoxazine-2,4,6-trione), XXIX

The bulk of the reaction mixture 1-B2 (unsublimed) melted between 214 and 300°C. It was soluble in methanol. About 21% of this material would not dissolve when extracted with ether. This ether-insoluble portion, 1-B3, mp 300-370°C, may be impure XVII. Its infrared spectrum (Figure 23) closely resembles that of 1-A1 (Figure 20), but its %C value of 70.67 is much lower. Therefore, an attempt was made to purify 1-B3, by recrystallization from alcohol. Three crops of material were obtained: 1-B4, mp 331-334°C; 1-B5, mp 330-333°C; and 1-B6, mp > 360°C. Their infrared spectra are identical (Figures 24, 25, and 26) to one another and to those from 1-A1 and 1-B3 (Figures 20 and 23) described above.

All of these materials probably have the same structure. Analytical results suggest that 1-B4, 1-B5, and 1-B6 may have an empirical formula approximating that of $C_{21}H_{13}O_2N_3$ (mol. wt. 339), and a structure as represented by XVII in the scheme in Figure 8. This could have resulted from the dehydration of the cyclotrimeric amide XVI. Obviously then, the formation of XVI could have occurred through a recombination of free radicals of the type A (cf Figures 4 and 8) after loss of carbon dioxide from [2H],3,1-benzoxazine-2,4-[1H]-dione, XV. None of the cyclotrimeric amide, XVI, was isolated.

The remainder of the material was isolated from the ether filtrate after the extraction of 1-B2. It melted at 177-200°C, and was also purified by recrystallization from alcohol. Three crops were obtained: 1-C1, mp 251-253°C; 1-C2, mp 248-251°C; 1-C3, mp 244-249°C; and 1-C4, mp 230-235°C. Their infrared spectra (Figures 27, 28, 29, and 30) are identical and exhibit two bands, one at 1709 cm^{-1} (medium), and the other

at 1681 cm^{-1} (strong) which can be attributed to carbonyl absorption. Presumably these cuts are the same material in varying degrees of purity. Since their infrared spectra closely resemble those from 2-A3B and 2-A3C (Figures 37 and 38), which have been identified as XVIII, it can be inferred that the products are impure samples of the cyclotetrameric amide, XVIII. Analytical values lie between those calculated for the cyclotetramer, XVIII, and its dehydration product, XIX.

On the basis of infrared spectral data, analytical data, and melting-point ranges, it would appear obvious that at least two different types of products are produced by the thermal decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV:

$\text{C}_{21}\text{H}_{13}\text{O}_2\text{N}_3$	mp $300\text{--}360^\circ\text{C}$	XVII
$\text{C}_{28}\text{H}_{20}\text{O}_4\text{N}_4$	mp $230\text{--}235^\circ\text{C}$	XVIII

In an attempt to isolate and identify pure samples of the components of the reaction mixture, a combination of extraction, sublimation, and chromatographic absorption techniques were employed. After a second run at 350°C for 22 days, the entire reaction mixture, including the material which sublimed on the walls of the flask, was extracted with ether. About 70% of the material was soluble. The ether-soluble material, 2-A, was subsequently extracted with benzene, in which all but a very small amount was soluble. The benzene-insoluble product, 2-A1, mp $295\text{--}300^\circ\text{C}$, had an infrared spectrum (Figure 31) strongly resembling those (Figures 23, 24, 25, and 26) from ether-insoluble products 1-B3 through 1-B6, described and identified above as XVII. This compound, 2-A1, was further

"purified" by sublimation under reduced pressure in a sublimation apparatus up to 360°C at 0.02 mm. The yellow sublimate, 2-A1A, mp 301-302°C appears to be a slightly purer version of 2-A1 since both have identical infrared spectra (Figures 32 and 31). The molecular-ion constant appears in the mass spectrum of 2-A1A at m/e 339. Based on the relative abundances of the ions at m/e 339 and m/e 340 at 100/23, and on the known isotopic ratio $^{13}\text{C}/^{12}\text{C}$ at 0.0112, the number of carbon atoms in the molecule was calculated to be 21. Its mass spectrum is shown in Figure 33. Analytical data shows that its values for %C, %H, and %N approach those calculated for the structure $\text{C}_{21}\text{H}_{13}\text{O}_2\text{N}_3$, XVII; mol. wt. 339. Also, since its infrared spectrum appears to be identical to those (Figures 24, 25, and 26) from 1-B4, 1-B5, and 1-B6, all these products probably have the structure XVII. Recently, XVII, mp >300°C, was obtained by Chatterjee and Ganguly by condensation of anthranilic acid, I, with P_2O_5 in refluxing xylene (Reference 16).

The benzene-soluble portion, 2-A2, was "purified" by the addition of petroleum ether to the benzene solution. The light-yellow precipitate, 2-A3, mp 225-230°C appears to have an infrared spectrum (Figure 34) closely resembling those (Figures 31 and 32) from 2-A1 and 2-A1A except for two new bands in the carbonyl region at 1770 cm^{-1} (weak) and 1724 cm^{-1} (strong).

Attempts were made to purify 2-A3 by vacuum sublimation at 260-360°C at 0.01 mm. In two trials identical results were obtained. The products, 2-A4 (mp 210-215°C) and 2-A5 (mp 212-210°C), had identical infrared spectra (Figures 35 and 37). In both cases the molecular-ion constant

appeared in their mass spectra at m/e 458. Based on the relative abundance of the ions at m/e 458 and m/e 459 the number of carbon atoms in the molecule was calculated to be 28. Analytical data appears to be consistent with an empirical formula $C_{28}H_{18}O_3N_4$. This indicates that the compounds 2-A4 and 2-A5 probably have the structure XIX, which could have resulted from dehydration of XVIII. It is interesting to note that the intensity of the molecular-ion peak at m/e 458 is a great deal weaker than the line at m/e 440, suggesting that a rapid thermal dehydration of the sample may be taking place at the high temperature (i.e., 250°C) at which the sample had been introduced into the mass spectrometer. The mass spectrum of product 2-A4 is shown in Figure 36.

Since it seems probable that sublimation of 2-A3 resulted in dehydration, an attempt was made to isolate a pure sample of the main component of 2-A3 by preparative thin-layer chromatography. Silica coated glass plates (8 inches x 8 inches) containing fluorescent indicator were employed. The material 2-A3 was deposited in a narrow band from a benzene solution. The bands were developed with a mixture of ether (4) and tetrahydrofuran (1). Five so-called bands were observed under ultraviolet light. The products isolated from the first and fourth bands, i.e., 2-A3A and 2-A3D, were obtained in very small amounts. They are probably not the same material even though their infrared spectra (Figures 36 and 39) resemble each other. An insignificant amount of material, 2-A3E, was present in the fifth band. The bulk of the product was obtained from the second and third bands (which appear to overlap somewhat). These products, 2-A3B and 2-A3C, have identical infrared spectra (Figures 40 and 41). Weak bands appearing at 3226 cm^{-1}

and 2900 cm^{-1} are probably due to bonded -NH out-of-plane-bending vibrations. Two bands appear in the carbonyl region at 1724 cm^{-1} and at 1681 cm^{-1} . These spectra closely resemble those obtained from the products 1-C1, 1-C2, 1-C3, and 1-C4, except for the presence of a water band at 3500 cm^{-1} in 2-A3B and 2-A3C (Figures 27 - 30). Analytical results indicate that the simplest empirical formula which can be assigned to these products is $\text{C}_7\text{H}_5\text{ON}$. The molecular-ion peak appears in the mass spectrum of 2-A3C (Figure 42) at m/e 476. Its molecular weight was found by the VPO method in dioxane to be 516. Based on the relative abundance of the ions in its mass spectrum at m/e 476 and m/e 477 the number of carbon atoms was calculated to be 28. This appears to indicate that 2-A3B and 2-A3C have a molecular formula $\text{C}_{28}\text{H}_{20}\text{O}_4\text{N}_4$. Analytical results confirm this formula. Here again it was observed that the intensity of the molecular-ion peak at m/e 476 is much weaker in intensity than the line at m/e 458, and that the line at m/e 440 is much stronger in intensity than the line at m/e 458. Since, as before, the sample was introduced into the mass spectrometer at high temperature, i.e., 250° , a rapid thermal dehydration of the compound, $\text{C}_{28}\text{H}_{20}\text{O}_4\text{N}_4$, XVIII, to $\text{C}_{28}\text{H}_{18}\text{O}_3\text{N}_4$, XIX, and finally to $\text{C}_{28}\text{H}_{16}\text{O}_2\text{N}_4$, XX, can be expected. Hence, the structure of products 2-A3B and 2-A3C, $\text{C}_{28}\text{H}_{20}\text{O}_4\text{N}_4$, can probably be represented as the cyclotetrameric amide, XVIII, as shown in Figure 8.

The ether-insoluble material 2-B representing about 23% of the initial reaction product was extracted with benzene. The insoluble extracted material, 2-B1, mp $348\text{-}351^\circ\text{C}$, exhibited a molecular-ion peak at m/e 440 in its mass spectrum. Its mass spectrum is identical to that from 2-B1B, Figure 47. Based on the relative abundance of the ions at

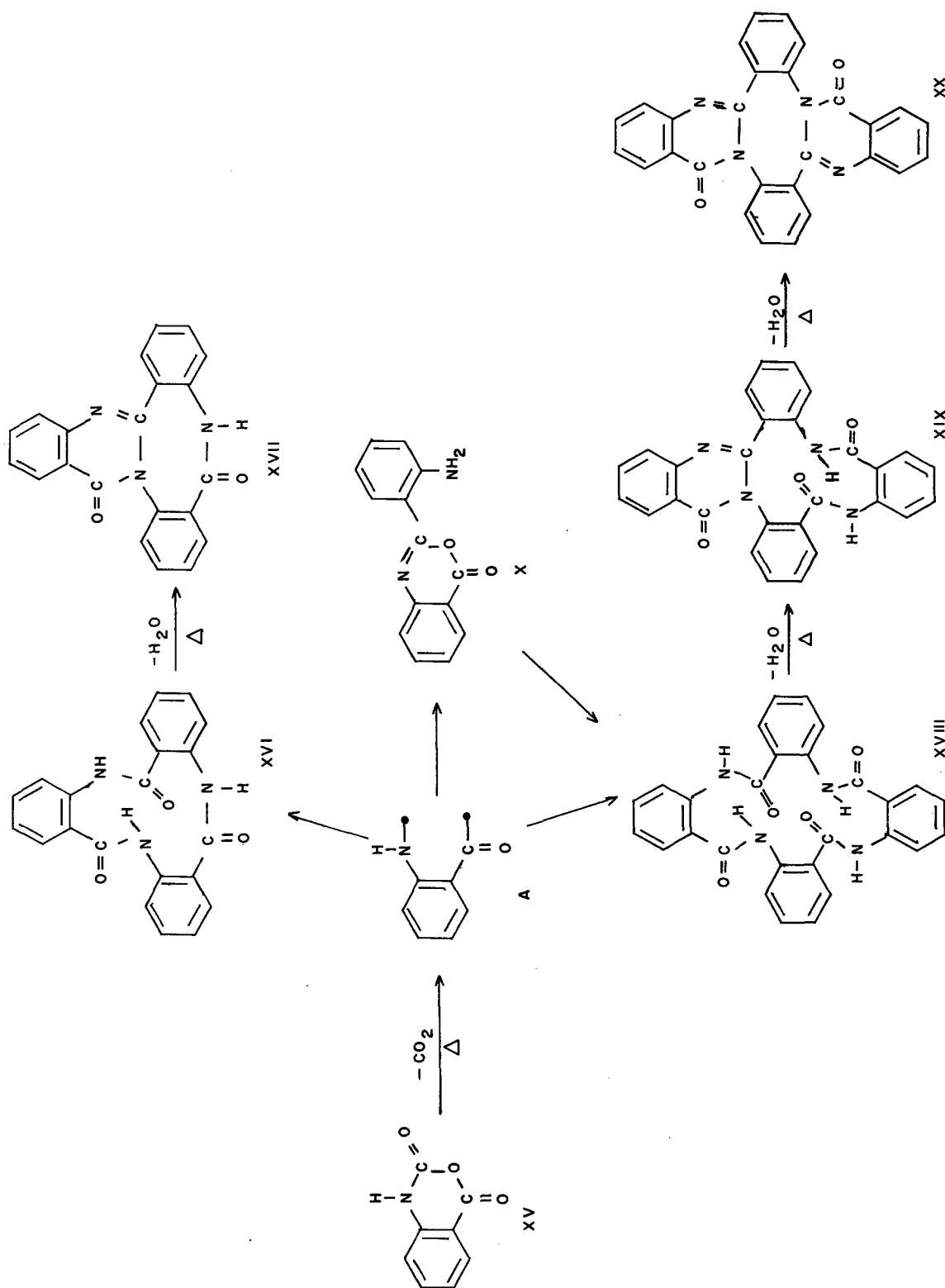


Figure 8. Products from Thermal Decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV

m/e 440 and at m/e 441, the number of carbon atoms in the molecule was calculated to be 28. This indicates that 2-B1 probably has a molecular formula $C_{28}H_{16}O_2N_4$ represented by structure XX of Figure 8, and that it results from the dehydration of XVIII initially to XIX and subsequently to XX. This has not been confirmed by analysis. Its infrared spectrum is shown in Figure 44. Its mass spectrum is identical to that from product 2-B1B (Figure 48).

An attempt was made to obtain a purer sample of 2-B1 by vacuum sublimation at $360^\circ\text{C}/0.02\text{ mm}$. The yellow sublimate, 2-B1A, mp $110\text{--}150^\circ\text{C}$, remained molten above 150°C but solidified again at $210\text{--}215^\circ\text{C}$. After further heating it remelted at $330\text{--}335^\circ\text{C}$. The molecular-ion constant appears in its mass spectrum at m/e 238. Based on the relative abundance of the ions in its mass spectrum at m/e 238 and m/e 239, the number of carbon atoms in the molecule was calculated to be 14. Its mass spectrum is shown in Figure 46. Since an even number of nitrogen atoms must be present, the lowest possible molecular formula which can be considered is $C_{14}H_{10}O_2N_2$. This would be agreeable for either dibenzo-[b,f][1,5]-diazocine-6,12-[5H,11H]-dione, XIV (Figure 4), or 2-o-aminophenylbenzoxazinone, X. Its infrared spectrum (Figure 45) exhibits two bands at 3344 cm^{-1} and 3333 cm^{-1} , indicating the presence of a free NH_2 group in the molecule. A strong band appearing at 1754 cm^{-1} is probably due to a carbonyl group in position 4 of the oxazine ring system (Reference 8). These results appear to agree with the infrared spectral data obtained by Kurihara (Reference 5) from a sample of 2-o-aminophenylbenzoxazinone, X, which he obtained by heating anthranilic acid in polyphosphoric acid at $140\text{--}150^\circ\text{C}$. Hence 2-B1A was identified as X.

The unusual melting behavior of product 2-B1A, X, suggests that it may be reacting with itself. Hence, the compound was heated in a tube under nitrogen at 250°C for two hours. The resulting product, 2-B1B, melted at 330-335°C. Its mass spectrum (Figure 48) exhibited the molecular-ion peak at m/e 440. Based on the relative abundance of the ions at m/e 440 and at m/e 441, the number of carbon atoms was calculated from the isotopic ratio $^{13}\text{C}/^{12}\text{C}$ to be 28. Since an even number of nitrogen atoms must be present, the closest molecular formula to be considered is $\text{C}_{28}\text{H}_{16}\text{O}_2\text{N}_4$, XX. These results show that 2-B1A (i.e., 2-o-aminophenylbenzoxazinone), X, self-condenses under nitrogen with elimination of water, to ultimately give the highly condensed product XX, probably through rearrangement to XVIII followed by dehydration to XIX and XX. Product 2-B1B as well as product 2-B2, which remained behind in the benzene solution after filtration of 2-B1, have infrared spectra (Figures 47 and 49) which appear to be identical to that from product 2B1 (Figure 44). Product 2-B2 melts at a considerably lower temperature, mp 295-300°C, than 2-B1 and is therefore probably an impure sample. Analytical results indicate that 2-B2 has a molecular formula approaching $\text{C}_{28}\text{H}_{16}\text{O}_2\text{N}_4$. This agrees fairly well with results from the mass spectrum of 2-B1B (Figure 48), where the molecular-ion constant was observed at m/e 440. Hence, the products, 2-B1, 2-B2, and 2-B1B can all be assigned structure XX, which is known as 10H, 21H-dibenzo-[3,4; 7,8][1,5]-diazocino-[2,1-b; 6,5-b']-diquinazoline-10, 21-dione. It is interesting to note that in addition to XVII, Chatterjee and Ganguly obtained a 2% yield of XX by self-condensation of anthranilic acid, I, with P_2O_5 in refluxing xylene (Reference 16).

The thermal decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV, at 360°C, therefore involves the initial loss of CO₂ and the formation of the diradical A (Figure 8) or the ketenamine [A] (Figure 9) in substantial amounts (Reference 13). Recombination of A or [A] leads to the formation of 2-o-aminophenylbenzoxazinone, X, and the cyclotrimeric and cyclotetrameric amides XVI and XVIII. At the high temperature of the reaction, and under conditions of vacuum distillation at 250°C, the dehydration of XVI and XVIII takes place to give a mixture of XVII, XIX, and XX.

The formation of the cyclotrimeric and cyclotetrameric amides, XVI and XVIII, from the thermal decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV, contrasts with the work reported by Smalley and Suschitzky, who studied the thermolysis of XV in boiling 1-methyl naphthalene at 243-245°C (Reference 13). These authors observed the slow liberation of carbon dioxide during the reaction and obtained a 20% yield of 2-o-aminophenylbenzoxazinone, X. The formation of this compound was explained by intermediary existence of the ketenamine, [A], which, behaving as a diene, reacts with another molecule of itself functioning as a dienophile. Their postulated reaction scheme is shown in Figure 9.

The products from the thermal decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV, are illustrated in Figure 8. No dibenzo-[b,f][1,5]-diazocine-6,12,[5H,11H]-dione, XIV, or any higher molecular weight polyamide, XXI, were isolated. No [5H]-dibenzo-[b,e][1,4]-diazepin-6-one, V, or dihydrophenazine, XXIII, or polymers therefrom (i.e., XXII or XXIV) were obtained (Figure 4).

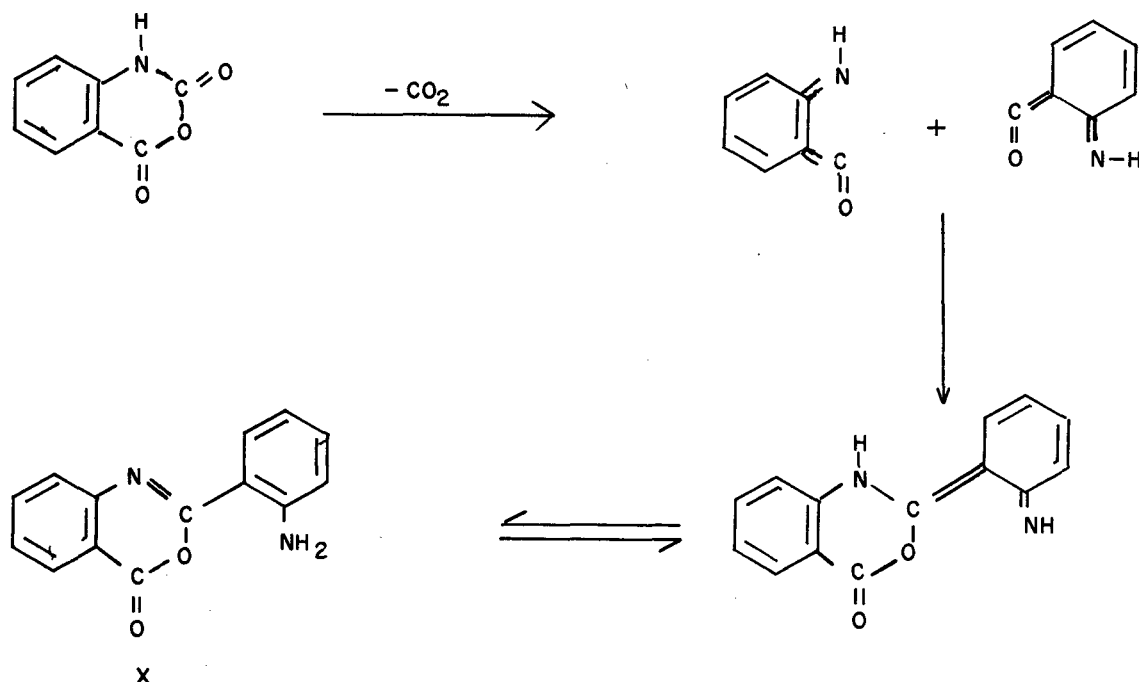


Figure 9. Scheme for the Thermal Decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV, in Boiling 1-methylnaphthalene by Smalley and Suschitzky (Reference 13)

To determine whether a soluble ladder polymer such as that illustrated by structure XXXI in Figure 5 could be obtained, the thermal decomposition of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI, was carried out. Here, of course, the possibility of obtaining structures similar to XXXII, XXXIII, or XXXIV was discounted since the results of the model reaction indicated that only CO_2 was eliminated from XV, and that the polymerization process involved the recombination of A radicals (Figures 3 and 7).

When compound XXVI was heated under nitrogen at 360°C for 21 days, a dark brownish-black polymer was obtained. It was insoluble in concentrated sulfuric acid and in methane sulfonic acid, and is probably cross-linked. Analytical results point to a molecular formula approaching

$C_{32}H_{16}O_7N_8$. Its infrared spectrum is shown in Figure 50. The product could have resulted from dehydration of an initial polyamide, $C_{32}H_{16}O_8N_8$, XXXIX, by loss of one molecule of water. Such a structure, XL, is illustrated in Figure 10. The reaction was run again, this time at $350^\circ C$ for 22 days. Analytical results indicated that this second product probably had a molecular formula near $C_{32}H_{12}O_6N_8$. This appears to suggest a further dehydration step involving loss of another molecule of water from $C_{32}H_{14}O_7N_8$, XL, to the more highly condensed product $C_{32}H_{12}O_6N_8$, XLI. Its infrared spectrum is shown in Figure 52. Although the structures of the reaction products from the thermal decomposition of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI, cannot be definitely postulated with certainty, structures representative of the products and their possible method of formation are depicted in Figure 9. The TGA curve of $C_{32}H_{14}O_7N_8$, XL, is shown in Figure 51 and indicates the product has good thermal stability. The beginning of degradation is evidenced by early weight loss near $400^\circ C$ with 80% weight residue remaining at $600^\circ C$ and 57.5% weight residue remaining at $900^\circ C$.

Next, the thermal decomposition of 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX, under nitrogen at $360-375^\circ C$ for 21 days was run. This product also was insoluble in concentrated sulfuric acid and in methane sulfonic acid, and is probably cross-linked. Analytical data indicates that the product has a molecular formula approaching $C_{28}H_{12}O_2N_4$, suggesting that it is highly condensed and may have resulted from dehydration of the corresponding initial polyamide $C_{28}H_{16}O_4N_4$, XLII, through the intermediary $C_{28}H_{14}O_3N_4$, XLII, by loss of two molecules of water. A structure representative of the product $C_{28}H_{12}O_2N_4$, XLIV, is

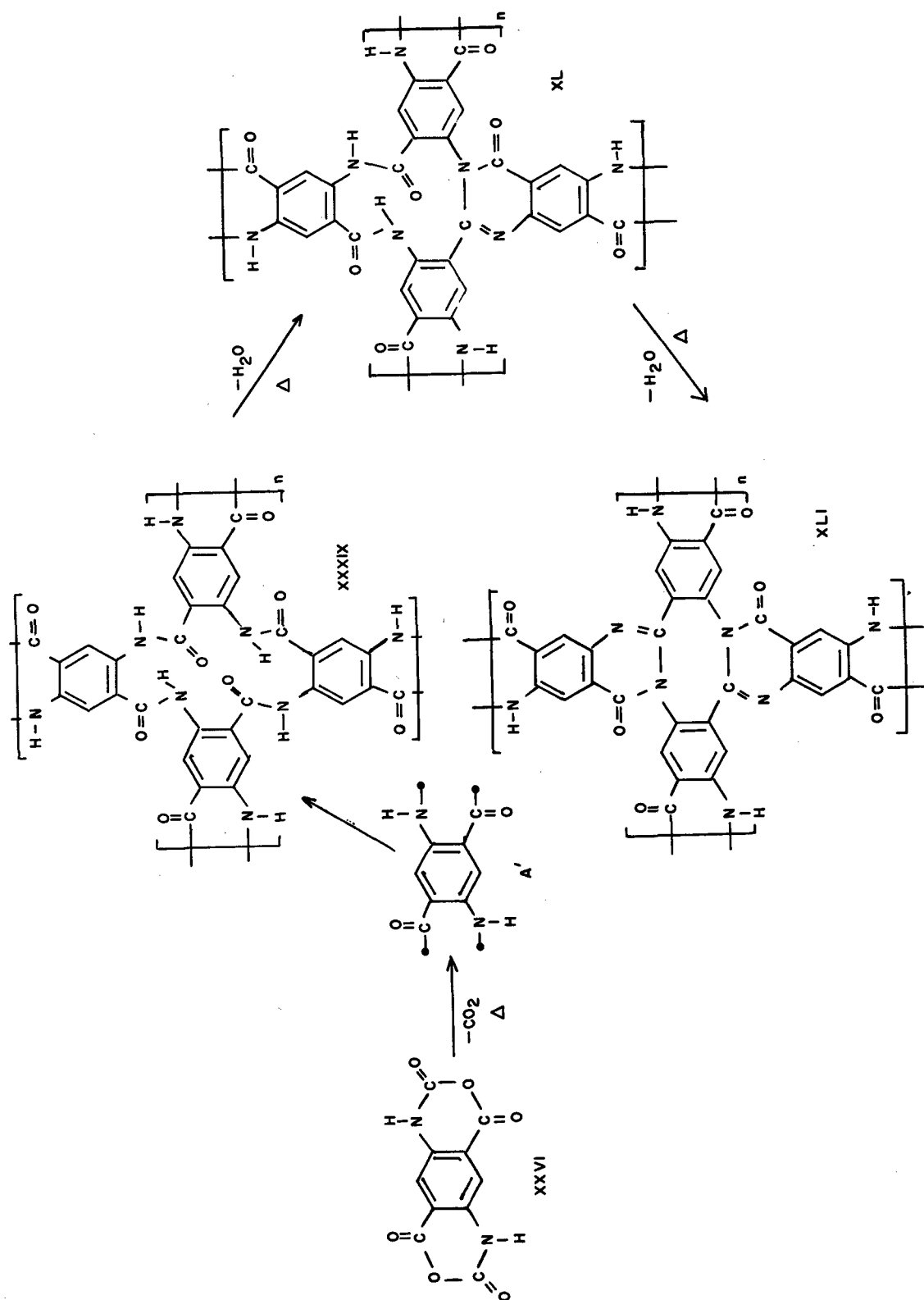


Figure 10. Products from Thermal Decomposition of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,11,6H]-tetraone, XXIII

depicted in Figure 11 along with its possible mode of formation. Its infrared spectrum is shown in Figure 53 and appears to be consistent for a material of amide character with a strong band due to carbonyl (amide I) appearing at 1680 cm^{-1} . The material appears to have a high degree of thermal stability. Its TGA curve, Figure 54, shows the beginning of degradation appearing as early weight loss at $500\text{-}600^{\circ}\text{C}$, with 78% weight residue remaining at 900°C .

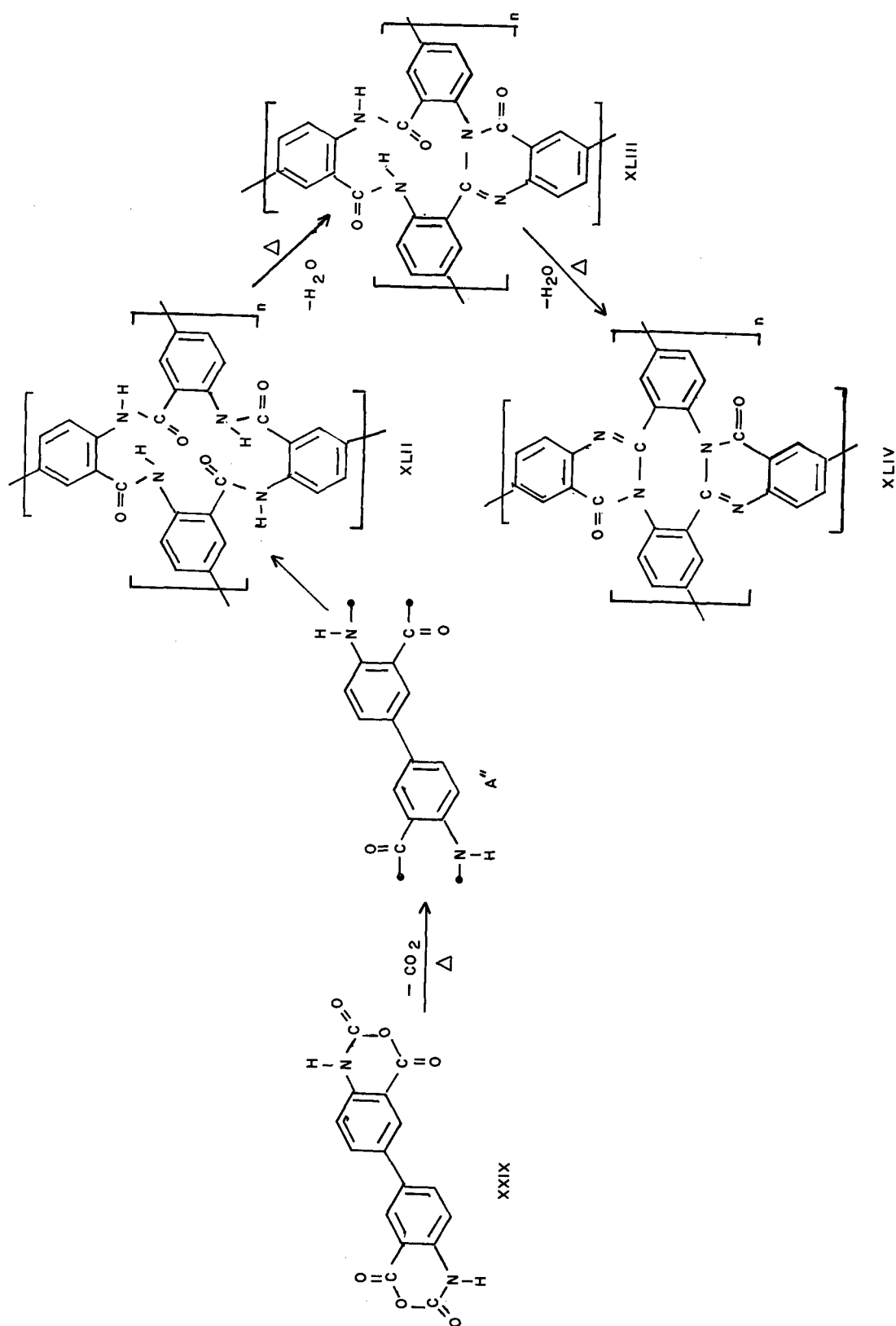


Figure 11. Products from Thermal Decomposition of 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX

SECTION III

CONCLUSIONS

1. The thermal decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione at 360°C involves loss of carbon dioxide followed by recombination of the radicals to produce cyclotrimeric and cyclotetrameric amides as the chief initial products.
2. Dehydration of the initial cyclic amides occurs on prolonged heating or during vacuum sublimation to give, ultimately, highly condensed structures related to the eight-membered diazocine ring system.
3. The thermal decomposition of difunctional derivatives such as [2H,7H],3,1,8,6-benzobisoxazine,2,4,7,9,[1H,6H]-tetraone, and 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione) conducted as a "melt" polymerization results in the formation of highly condensed structures related to those from [2H],3,1-benzoxazine-2,4,[1H]-dione. Although these products exhibit a high degree of thermal stability, they are insoluble cross-linked materials.
4. "Melt" reactions involving the thermal decomposition of tetraones related to [2H],3,1-benzoxazine-2,4,[1H]-dione cannot be used to produce soluble, useful polymers containing the eight-membered diazocine ring system.

SECTION IV
RECOMMENDATIONS

1. Work involving melt decomposition of difunctional derivatives related to [2H],3,1-benzoxazine-2,4,[1H]-dione will be terminated.
2. Reactions involving the formation of soluble linear polybenzoxazinones and their subsequent modification to a highly condensed diazocine structures should be investigated.

SECTION V
EXPERIMENTAL

1. General Comments

a. Starting Materials

[2H],3,1-benzoxazine-2,4,[1H]-dione (isatoic anhydride), was prepared from anthranilic acid, I, by reaction with phosgene in concentrated hydrochloric acid (References 9 and 10).

[5H]-dibenzo-[b,e][1,4]-diazepin-6-one, V, was prepared by the ring closure of 2-aminodiphenylamine-6'-carboxylic acid, IV, in refluxing xylene (Reference 1).

2-aminodiphenylamine-6'-carboxylic acid, IV, was obtained by reduction of 2-nitrodiphenylamine-6'-carboxylic acid, III, with ferrous sulfate in concentrated ammonium hydroxide (Reference 1).

2-nitrodiphenylamine-6'-carboxylic acid, III, was prepared by reaction of anthranilic acid, I, with o-chloronitrobenzene, II, in the presence of K_2CO_3 and copper powder at 200°C (Reference 1).

Anthranilic acid, I (Eastman No. 29), and o-chloronitrobenzene, II (Eastman No. 70), were obtained from Distillation Products Industries, Rochester, New York.

b. Infrared Spectra

The infrared spectra were obtained by use of a Perkin-Elmer Model 521 Infrared Spectrophotometer from KBr pellets prepared by the window technique (Reference 11).

c. Thermogravimetric Analyses

Thermogravimetric analyses were obtained by heating 50 to 100 mg of the compound under nitrogen in a Chevenard Thermobalance (Adamel, Paris, France) to 900°C at a heating rate of 180°C per hour.

d. Softening Point Determinations

The softening characteristics of the compounds were obtained by means of a modified Vicat apparatus (Reference 12). Heating was performed at a constant rate of 150°C per hour. The softening range was determined from a plot of temperature vs penetration.

e. High Resolution Mass Spectrometry

The compounds were introduced via the direct introduction probe at temperatures from 130 up to 250°C, depending on the run into a CEC Model 21-110B Mass Spectrometer at ionizing voltage of 70 eV and an accelerating voltage of 8 kV.

2. Preparation and Polymerization of Monomers

a. [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI

A solution was prepared from 4.5 g of 2,5-diamino terephthalic acid, 200 ml of concentrated hydrochloric acid, and 500 ml of water. The solution was cooled below 20°C and phosgene was bubbled through the

solution over a six to eight hour period, until about 55 g had been added. The yellow solid product which had precipitated was filtered off, washed with water, and suction dried; yield 3.5 g. The product was recrystallized from 150 ml of dimethyl acetamide and dried in a vacuum pistol at 100°C/0.01 mm for 24 hours. The product appears to decompose without melting above 330°C. Its softening point curve is illustrated in Figure 14, and its infrared spectrum is shown in Figure 13.

Anal. Calc'd for $C_{10}H_4O_6N_2$, XXVI: %C, 48.39; %H, 1.63; %N, 11.29; Mol. Wt., 248.2
 Found : %C, 48.51; %H, 1.77; %N^D, 11.09; Mol. Wt.* , 241.4

(Note: * denotes molecular weight by the VPO method in DMF at 37°C.)

b. 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX

A solution was prepared from 6 g of benzidine-3,3'-dicarboxylic acid, XXVIII, and 55 g of sodium bicarbonate in one liter of water. The solution was treated with charcoal and filtered to remove most of the dark color. The filtrate was stirred at 10°C, and phosgene was passed through the solution over a period of four hours. A yellowish-white product precipitated gradually. The solid was filtered off and washed with water, dilute acetic acid, methanol, and finally, petroleum ether; yield 5.8 g. Five grams of the crude product was dissolved in 500 ml of boiling dimethylacetamide. The compound dissolved slowly with difficulty. No precipitation occurred on cooling. The solution was frozen in dry ice and then thawed. The finely divided yellowish-white solid was filtered off, washed with methanol, and dried at 100°C/0.1 mm for 24 hours; yield 2.2g. The compound apparently decomposes without melting above

D - nitrogen by the Dumas method

360°C. Its softening point curve is illustrated in Figure 16 and its infrared curve in Figure 15.

Anal. Calc'd for $C_{16}H_8O_6N_2$, XXIX : %C, 59.26; %H, 2.49; %N, 8.61

Found : %C, 59.21; %H, 2.70; %N^D, 8.63

3. Thermal Decomposition of [2H],3,1-benzoxazine-2,4,[1H]-dione, XV

a. Run No. 1

[2H],3,1-benzoxazine-2,4,[1H]-dione, XV, 4.89 g, (0.03 mole), was heated in a tube, 25 mm x 140 mm at 250°C in a stream of nitrogen for 21 days. The tube was heated in an aluminum block encased in a Glas-col-heating mantle. The temperature was controlled by means of a Thermocap relay. A small amount of yellow solid, 1-A, sublimed on the upper walls of the tube and adaptor; yield 0.95 g. It was scraped into a beaker and stirred with 125 ml of cold methanol. Most of it dissolved to give a clear yellow solution. The small amount of yellowish-white insoluble material, 1-A1 was filtered off and dried; yield 0.9 g. This product was insoluble in DMF (dimethyl formamide). Its infrared spectrum is shown in Figure 20.

Anal. Calc'd for $C_{21}H_{13}O_2N_3$, XVIV: %C, 74.32; %H, 3.86; %N, 12.38

Found : %C, 74.48; %H, 4.16; %N^D, 13.00

The residue in the tube, 1-B, 2.94 g was broken up and stirred with 250 ml of hot methanol in which it was almost completely soluble. The small amount of insoluble material, 1-B1, was filtered off and dried at 100°C/0.05 mm (yield 0.01 g). Its infrared spectrum is shown in Figure 21.

D - nitrogen by the Dumas method

The methanol filtrate from 1-B1 was evaporated to a yellow residue 1-B2. The material was dried at 100°C/0.05 mm; yield 2.8 g, mp 214-300°C. Its infrared spectrum is shown in Figure 22. It was extracted with four 200 ml portions of ether. The ether insoluble portion 1-B3 was filtered off and dried at 100°C/0.1 mm; yield, 0.6 g, mp 334-360°C. Its infrared spectrum is shown in Figure 23.

Anal. Calc'd for $C_{21}H_{13}O_2N_3$, XVII: %C, 74.32; %H, 3.86; %N, 12.38

Found : %C, 70.67; %H, 4.01; %N^D, 14.04

1-B3 was dissolved in 400 ml of warm alcohol. The solution was treated with charcoal and filtered. The filtrate after alternate evaporation and cooling gave successive crops of product; 1-B4, yield 0.21 g, mp 331-334°C; 1-B5, yield 0.16 g, mp 330-333°C; 1-B6, yield 0.11 g, mp > 360°C. Their infrared spectra are shown in Figures 24, 25, and 26.

Anal. Calc'd for $C_{21}H_{13}O_2N_3$, XVII: %C, 74.32; %H, 3.86; %N, 12.38;

Mol. Wt., 339

Found 1-B4 : %C, 74.36; %H, 3.82; %N^D, 13.04;

Mol. Wt., 597*

Found 1-B5 : %C, 74.21; %H, 4.11; %N^D, 12.72

Found 1-B6 : %C, 75.03; %H, 4.06; %N^D, 16.25

(Note: *denotes molecular weight by the VPO method in DMF at 130°C.)

The ether filtrate from product 1-B3 was evaporated to a yellow residue, C, and dried at 100°C/0.1 mm; yield 2.0 g, mp 177-200°C. It

D - nitrogen by the Dumas method

was soluble in benzene, chloroform, acetone, dioxane, ether, and warm alcohol, and insoluble in hexane, or cyclohexane. C was dissolved in 50 ml of alcohol. The solution was treated with charcoal and filtered. Treatment of the filtrate with successive 25 ml portions of water gave four crops of material, 1-C1, yield 0.8 g, mp 251-253°C; 1-C2, yield 0.52 g, mp 248-251°C; 1-C3, yield 0.34 g, mp 244-249°C; 1-C4, yield 0.11 g, mp 230-235°C. Their infrared spectra are shown in Figures 27, 28, 29, and 30.

Anal. Calc'd for $C_{28}H_{18}O_3N_4$, XIX: %C, 73.34; %H, 3.96; %N, 12.22;

Mol. Wt. 458

$C_{28}H_{20}O_4N_4$, XVIII: %C, 70.50; %H, 4.23; %N, 11.78;

Mol. Wt. 476

50% XVIII and XIX: %C, 72.00; %H, 4.07; %N, 12.00;

Mol. Wt. 467

Found	1-C1	:	%C, 72.06; %H, 3.88; %N ^D , 12.72
	1-C2	:	%C, 72.53; %H, 4.11; %N ^D , 12.31
	1-C3	:	%C, 74.13; %H, 4.09; %N ^D , 12.11;
			Mol. Wt. 471*
	1-C4	:	%C, 73.75; %H, 4.03; %N ^D , 12.75;
			Mol. Wt. 485*

(Note: * denotes molecular weight by VPO method in DMF at 130°C.)

b. Run No. 2

[2H], 3,1-benzoxazine-2,4,[1H]-dione, XV, 4.89 g (0.03 mole) was decomposed at 250°C under nitrogen over 21 days. The reaction mixture,

D - nitrogen by the Dumas method

4.05 g was extracted with 200 ml of ether. The ether-insoluble material 2-B was filtered off and vacuum dried at 80°C/0.01 mm; yield 0.65 g. The ether filtrate (after charcoal treatment) was evaporated leaving behind a yellow residue 2-A; yield 2.74 g.

This yellow residue, 2-A, was completely soluble in acetone, methanol and dioxane, but insoluble in ligroin and cyclohexane. It was nearly all soluble in benzene and after stirring in this solvent for fifteen minutes, a small amount of granular solid, 2-A1, was filtered off and dried; yield, 0.05 g. Its infrared spectrum is shown in Figure 31. It appears to melt in the range of 295-300°C.

The clear yellow benzene filtrate after separation of 2-A1 was evaporated in a tared dish at 50°C in the hood to a yellow residue, 2-A2; yield, 2.11 g. This solid was redissolved in 50 ml of benzene, and this solution was treated with 200 ml of ligroin (30-60) giving a yellow precipitate 2-A3; yield 2.0 g. It melts in the 225-230°C range. Its infrared spectrum is shown in Figure 34.

Meanwhile 2-B was stirred with cold benzene for one hour, then filtered. A white insoluble product 2-B1 was air dried; yield 0.25 g. It darkens above 320°C and shrinks and melts between 340 and 351°C. Its infrared spectrum is shown in Figure 44. What appears to be the molecular ion peak was observed in its mass spectrum at m/e 440, which is identical to that from 2-B1B (Figure 48).

The yellow filtrate from 2-B1 was evaporated in the hood over a hot plate at 50°C to a residue 2-B2; yield, 0.40 g. The product melts between 295 and 300°C. Its infrared spectrum is shown in Figure 49.

Anal. Calc'd for $C_{28}H_{16}O_2N_4$, XX: %C, 76.35; %H, 3.66; %N, 12.71;

Mol. Wt. 440

Found : %C, 75.41; %H, 3.75; %N^D, 12.57;

m/e 440

(1.) Sublimation of 2A-1

A sample of the product 2-A1 was heated in a sublimation apparatus up to 360°C at 0.02 mm for several hours. A light-yellow sublimate 2-A1A was obtained. It melted at 300-302°C. Its infrared spectrum is illustrated in Figure 31 and appears to be identical to that of the unsublimed material (Figure 30). Its mass spectrum was run. The molecular ion peak was located at m/e 339. Its mass spectrum is shown in Figure 33.

Anal. Calc'd for $C_{21}H_{13}O_2N_3$, XVII: %C, 74.30; %H, 3.88; %N, 12.40;

Mol. Wt. 339

Found : %C, 72.11; %H, 3.98; %N^D, 12.40;

m/e 339

(2.) Sublimation of 2A-3

A small sample of 2-A3 was heated in a sublimation apparatus at 260-360°C/0.01 mm. A yellow sublimate 2-A4 melting at 210-215°C was obtained. Its infrared spectrum is shown in Figure 35. What appears to be its molecular ion peak is observed at m/e 458 in its mass spectrum (Figure 36).

D - nitrogen by the Dumas method

Anal. Calc'd for $C_{28}H_{18}O_3N_4$, XIX: %C,73.34; %H,3.96; %N,12.22;

Mol. Wt. 458

Found : %C,71.09; %H,3.97; %N^D,12.72;

m/e 458

Since this small sample appeared to be impure, a larger sample of 2-A3 was sublimed in the same way, over a period of 6 hours. This sublimate, 2-A5, melted at 212-218°C. Its infrared spectrum (Figure 36) appears to be identical to that (Figure 37) from 2-A4. Its mass spectrum exhibits what appears to be its molecular ion constant at m/e 458.

Anal. Calc'd for $C_{28}H_{18}O_3N_4$, XIX: %C,73.34; %H,3.96; %N,12.22;

Mol. Wt. 458

Found : %C,72.46; %H,4.06; %N^D,12.16;

m/e 458

The unsublimed residue in the tube after removal of 2-A5 was extracted with acetone and filtered. Evaporation of the yellow filtrate left a yellow residue, 2-A5A. It began to shrink near 225°C and melted at 235-250°C to a viscous liquid. Its infrared spectrum is shown in Figure 38.

(3.) Sublimation of 2-B1

A small sample of 2-B1 was heated at 360°C/0.02 mm for 3-4 hours. An orange-yellow solid 2-B1A gradually sublimed. The compound began to shrink when heated near 100°C, melting to a clear liquid at 110-150°C. On further heating the liquid became opaque near 200°C becoming

D - nitrogen by the Dumas method

solid at 210-215°C. This new solid melted at 330-335°C. An infrared spectrum of 2-B1A is shown in Figure 45. The molecular ion constant appears in its mass spectrum at m/e 238. Its mass spectrum is shown in Figure 46.

Because of the unusual behavior of 2-B1A, it was heated for two hours under nitrogen at one atmosphere. The resulting product, 2-B1B, melted at 330-335°C. Its infrared spectrum is illustrated in Figure 47. What appears to be its molecular ion peak is exhibited in its mass spectrum at m/e 440. The mass spectrum is shown in Figure 48.

(4.) Preparative Thin-Layer Chromatography, Purification of 2-A3

Product 2-A3, 0.5 g was dissolved in 100 ml of benzene. The solution was placed in a band about one-half inch wide on an 8 inch x 8 inch preparative glass plate (Silica Gel F254, Merck Precoated, for PLC with fluorescent indicator, Brinkman Instruments). The solvent was evaporated. The plate was dried and then "developed" using a solvent mixture consisting of ether (4)-THF (1). What appeared to be five bands were observed under ultraviolet light. They were separately scraped off the plate and each was separately eluted with THF.

The products were recovered by evaporation of the solvent; yields: 2-A3A, 0.02 g; 2-A3B, 0.03 g; 2-A3C, 0.16 g; 2-A3D, 0.02 g; 2-A3E, < 0.01 g.

The infrared spectrum of 2-A3A is shown in Figure 39. A mass spectrum was run on this material but results were poor. It may be a mixture.

The infrared spectrum of 2-A3B is shown in Figure 40. It was different from that of 2-A3A above.

Anal. Calc'd for $C_{28}H_{20}O_4N_4$, XVIII: %C,70.50; %H,4.23; %O,13.42; %N,11.78
 Found : %C,69.94; %H,4.18; %O,14.04;%N^D,12.15

The infrared spectrum of 2-A3C is shown in Figure 41. It is identical to that (Figure 40) from 2-A3B described above. A mass spectrum was run on this product. The probe was introduced into the spectrophotometer at 250°C. A weak band believed to be its molecular ion constant appeared at m/e 476. A medium band was visible at m/e 458, while a strong band was evident at m/e 440. This suggests that the original material may be undergoing rapid dehydration at 250°C in the spectrometer first to a compound of molecular weight 458, then to a compound of molecular weight 440. A molecular weight determination was run on the product in dioxane by the VPO method, and the material was also analyzed. Its mass spectrum is shown in Figure 42.

Anal. Calc'd for $C_{28}H_{20}O_4N_4$, XVIII: %C,70.50; %H,4.23; %N,11.78;
 Mol. Wt. 476
 Found : %C,69.62; %H,3.85; %N^D,12.07;
 Mol. Wt. 516*; m/e, 476

(Note: * denotes molecular weight by the VPO method in dioxane.)

D - nitrogen by the Dumas method

4. Thermal Decomposition of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI

a. Run No. 1

A pyrex glass tube, 25 mm x 140 mm, was sealed at one end and fitted with a 24/40 female joint, and 0.496 g of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-dione was added. The tube was fitted with an adaptor for inlet and outlet of nitrogen. The apparatus was placed in the cavity of an aluminum block encased in a heating mantle. Nitrogen was passed through the apparatus in a slow stream and the apparatus was heated to 360°C. The temperature was controlled at 360°C by means of a Thermocap relay for 21 days. The product was a dark brownish-black granular solid; yield 0.3 g. The product was insoluble in dioxane, dimethyl formamide, dimethylsulfoxide, hexamethyl phosphoramide, concentrated sulfuric acid, and methane sulfonic acid. Its infrared spectrum and TGA curve are shown in Figures 50 and 51.

Anal. Calc'd for $C_{32}H_{16}O_8N_8$, XXXIX: %C,60.00; %H,2.51; %N,17.49

Calc'd for $C_{32}H_{14}O_7N_8$, XL : %C,61.65; %H,2.26; %N,18.03

Found : %C,61.15; %H,2.32; %N^D,19.76

b. Run No. 2

In the apparatus described above, 1.86 g of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone was heated at 350°C under nitrogen for 22 days. The product was a dark brownish-black powder; yield 1.06 g. It was insoluble in organic solvents and also insoluble

D - nitrogen by the Dumas method

in concentrated sulfuric acid, or methane sulfonic acid. Its infrared spectrum is shown in Figure 52.

Anal. Calc'd for $C_{32}H_{16}O_8N_8$, XXXIX: %C,60.00; %H,2.51; %N,17.49

Calc'd for $C_{32}H_{12}O_6N_8$, XLI : %C,63.60; %H,2.00; %N,18.53

Found : %C,63.24; %H,2.71; %N^K,19.00

5. Thermal Decomposition of 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione) XXIX

In the apparatus described above, 0.60 g of 6,6'-bis([4H],3,1-benzoxazine-2,4,[1H]-dione) was heated at 360-375°C under nitrogen for a period of 21 days. The product was a brownish-yellow solid; yield 0.50 g. It was insoluble in organic solvents and was also insoluble in methane sulfonic acid. Its infrared spectrum and TGA curve are shown in Figures 53 and 54.

Anal. Calc'd for $C_{28}H_{16}O_4N_4$, XLII: %C,71.25; %H,3.42; %N,11.88

Calc'd for $C_{28}H_{14}O_3N_4$, XLIII: %C,74.20; %H,3.17; %N,12.38

Calc'd for $C_{28}H_{12}O_2N_4$, XLIV: %C,77.00; %H,2.78; %N,12.85

Found : %C,77.22; %H,2.95; %N^D,13.25

D - nitrogen by the Dumas method

K - nitrogen by the Kieldahl method

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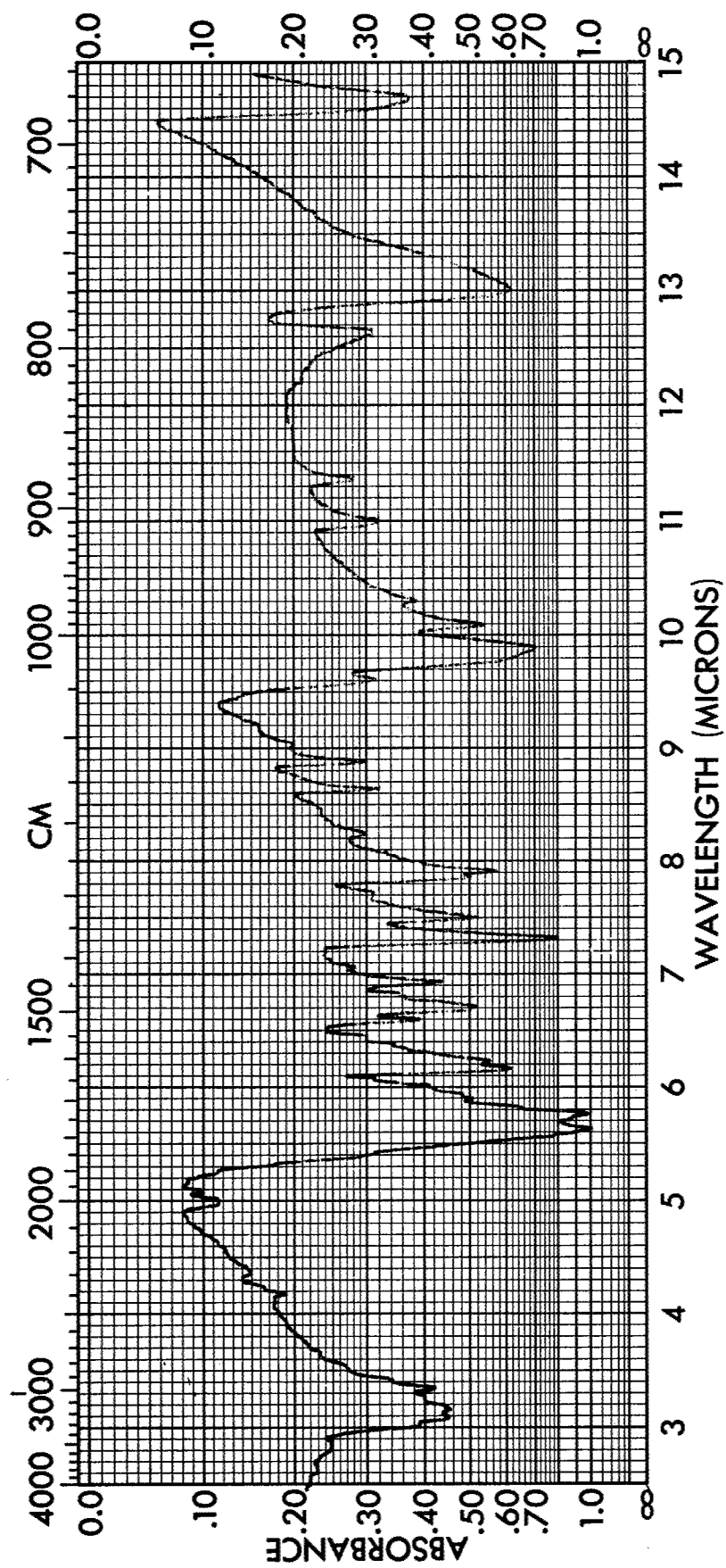


Figure 12. Infrared Spectrum of [2H], 3,1-benzoxazine-2,4,[1H]-dione (isatoic anhydride), XV

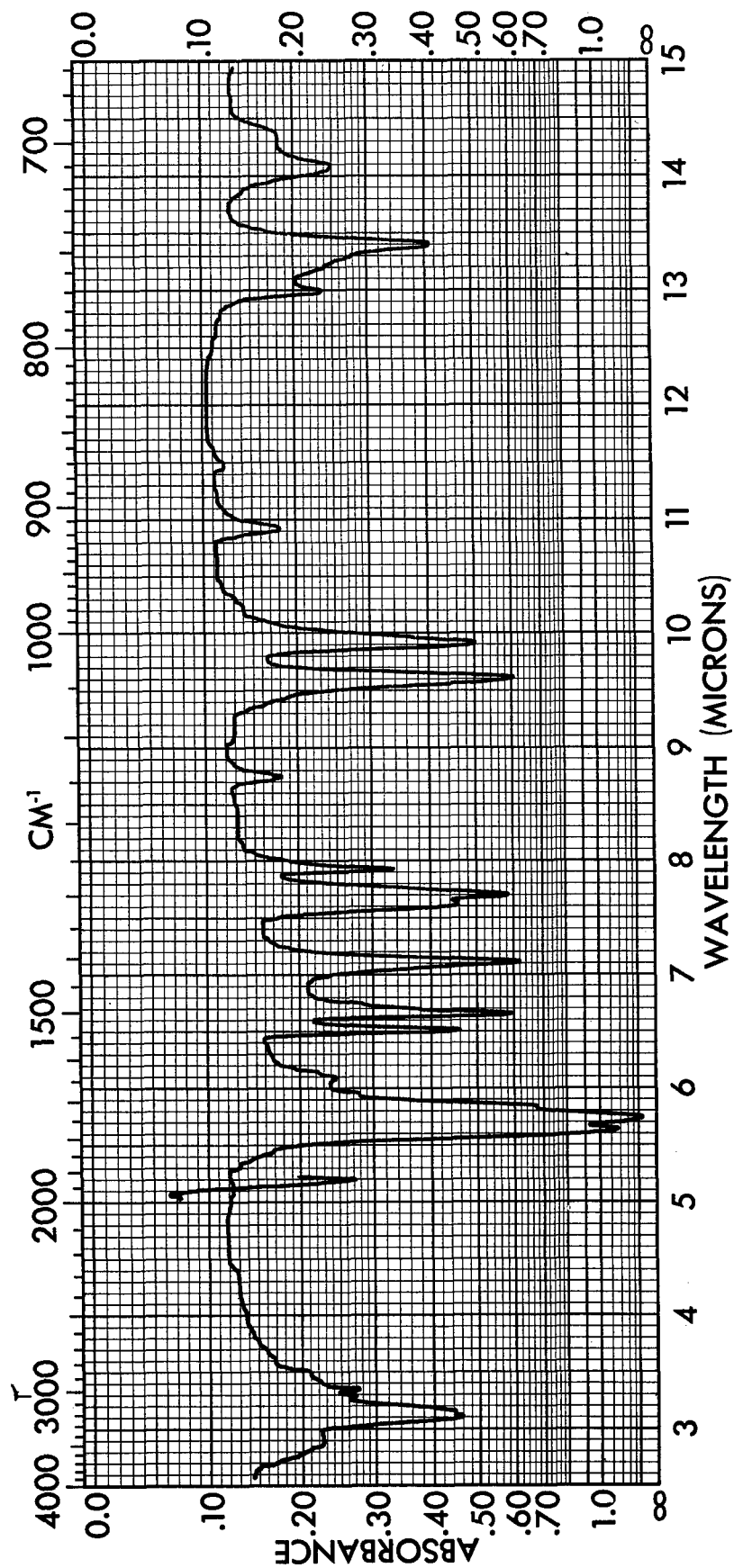


Figure 13. Infrared Spectrum of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI

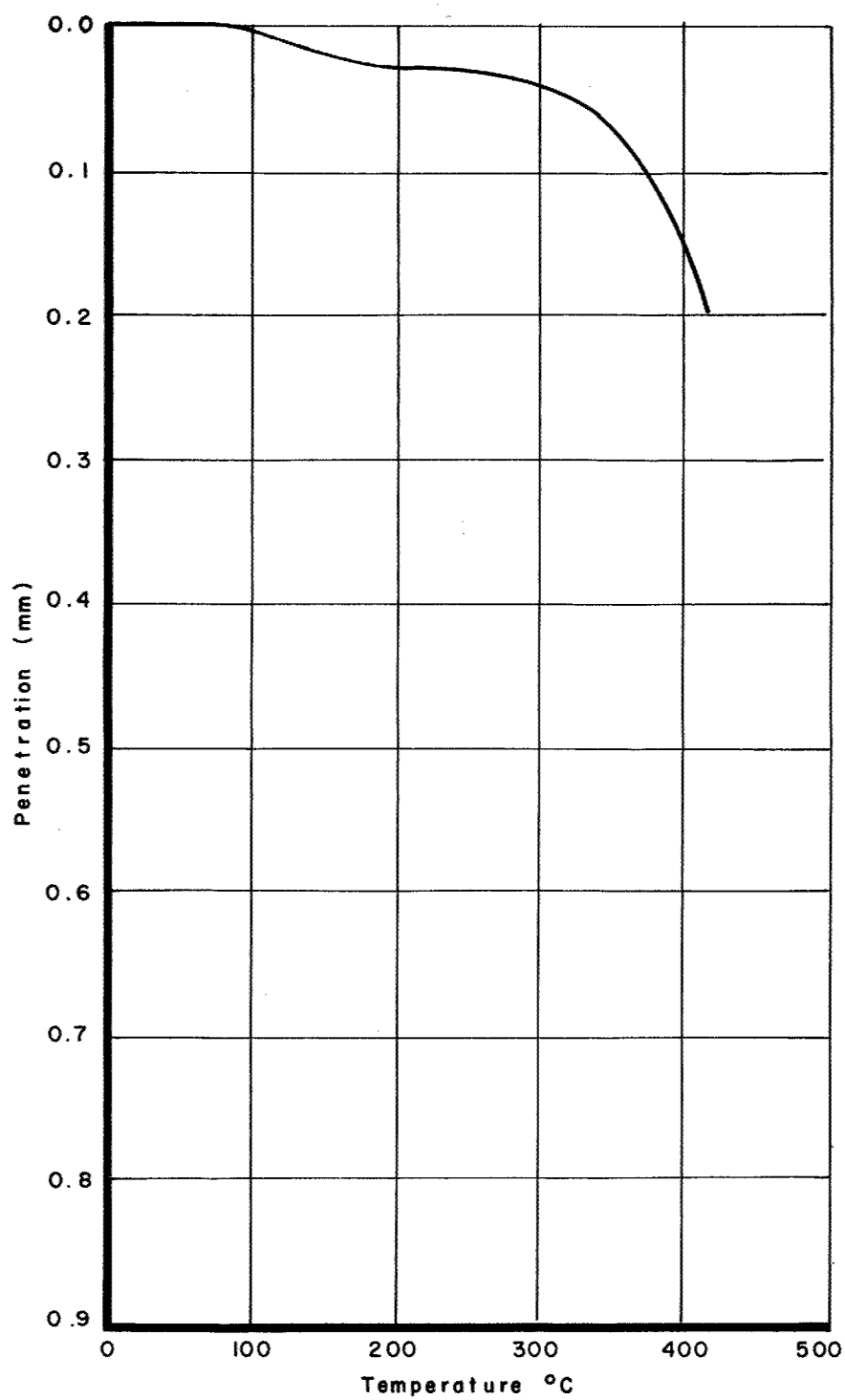


Figure 14. Softening Point Curve from [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI

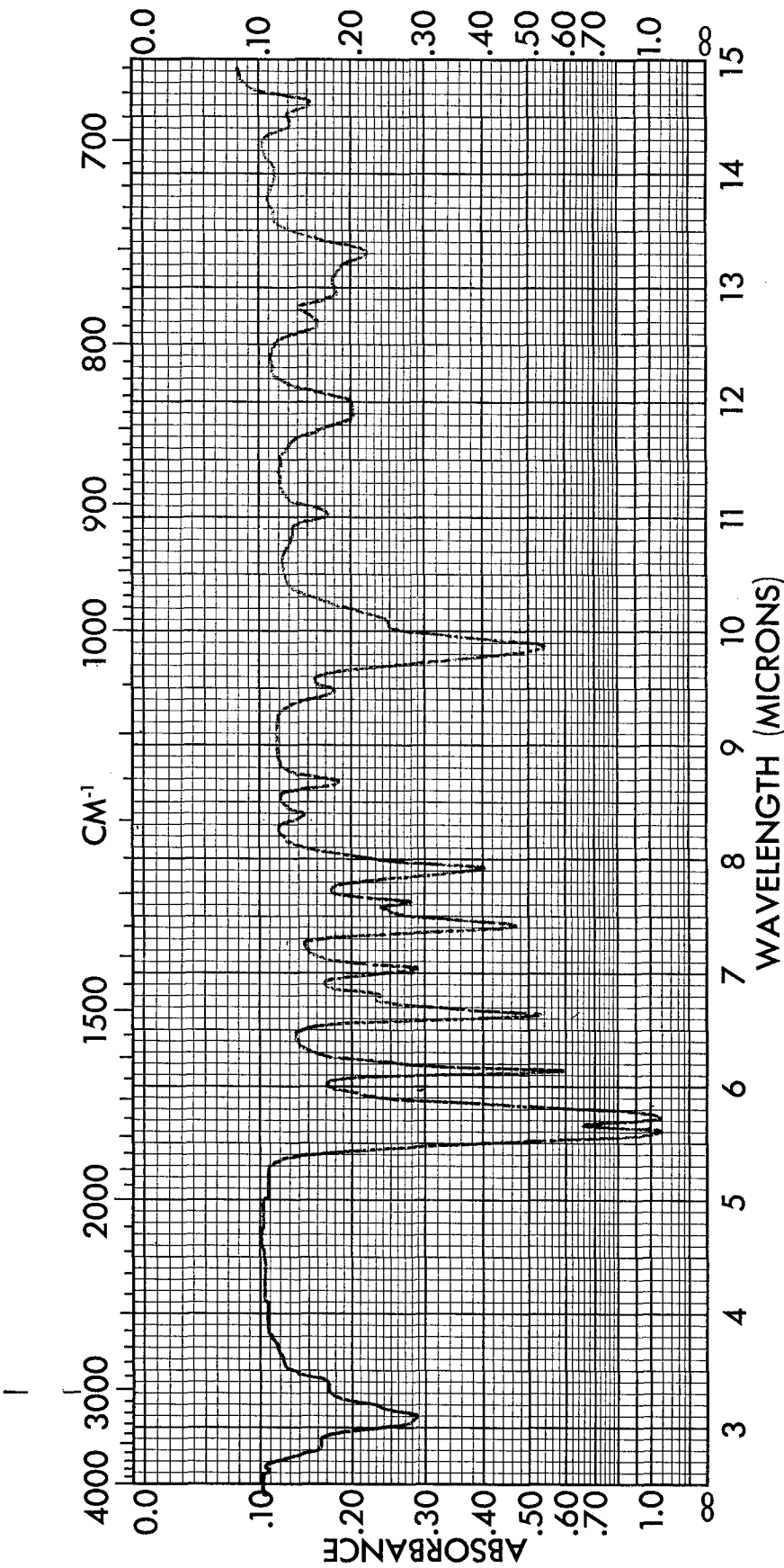


Figure 15. Infrared Spectrum of 6,6'-bis-([2H],3,1-benzoxazine-2,4, [1H]-dione), XXIX

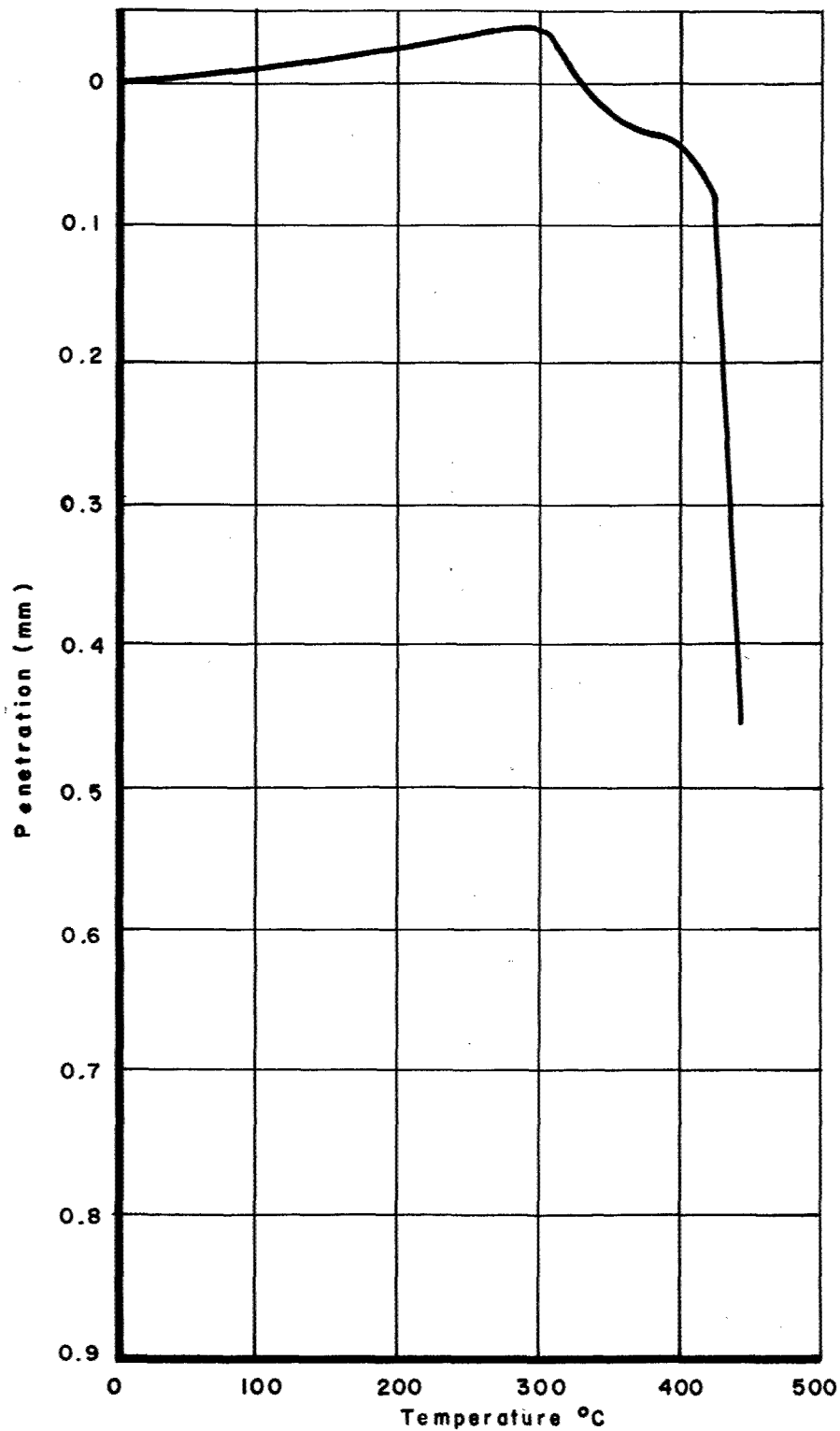


Figure 16. Softening Point Curve from 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX

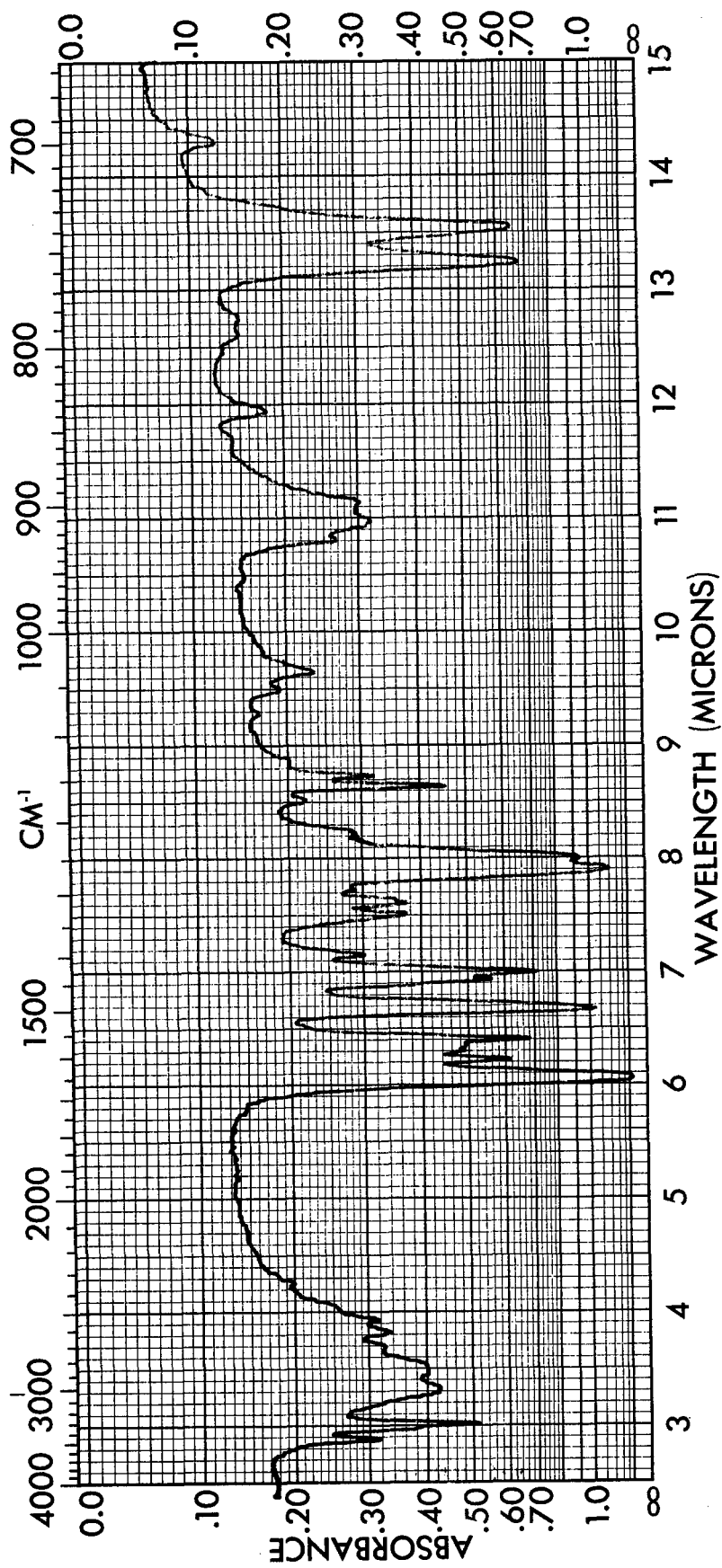


Figure 17. Infrared Spectrum of 2'-aminodiphenylamine-6'-carboxylic Acid, IV, mp 197-198°C

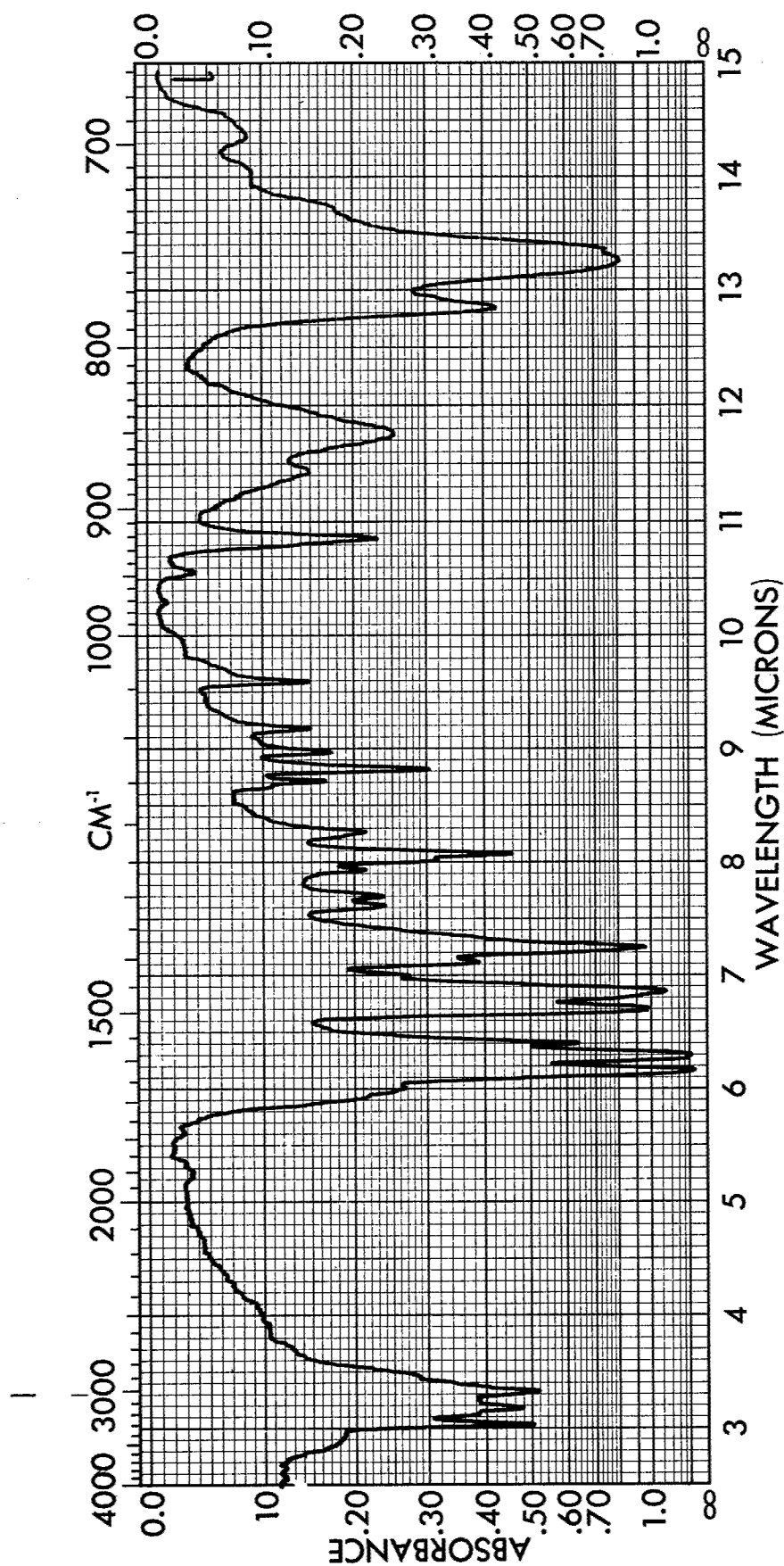


Figure 18. Infrared Spectrum of [5H]-dibenzo-[b,e][1,4]-diazepin-6-one, V, mp 245-247°C

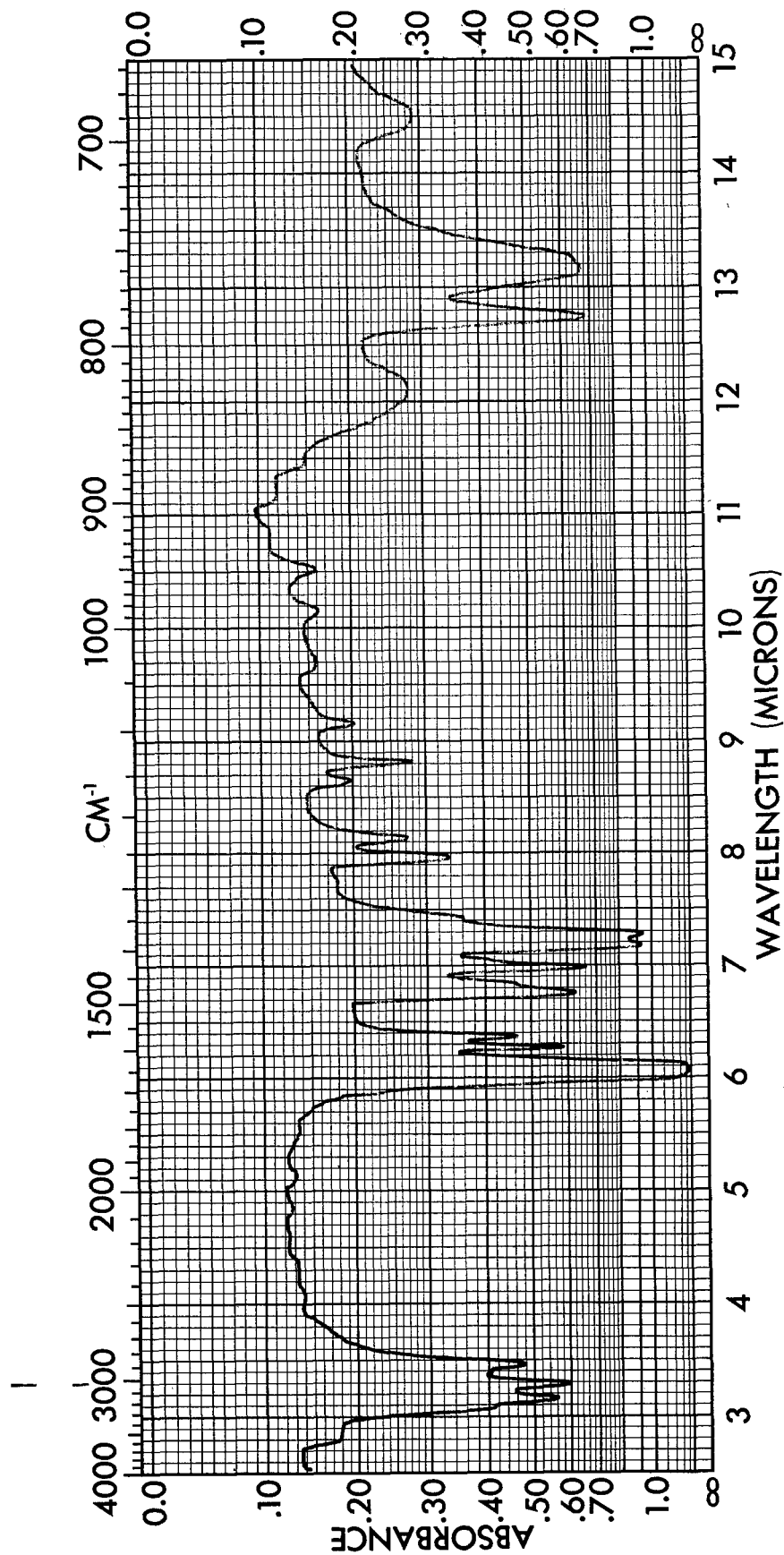


Figure 19. Infrared Spectrum of Dibenzo-[b,f][1,5]-diazocine-6,12,15H-dione, XIV

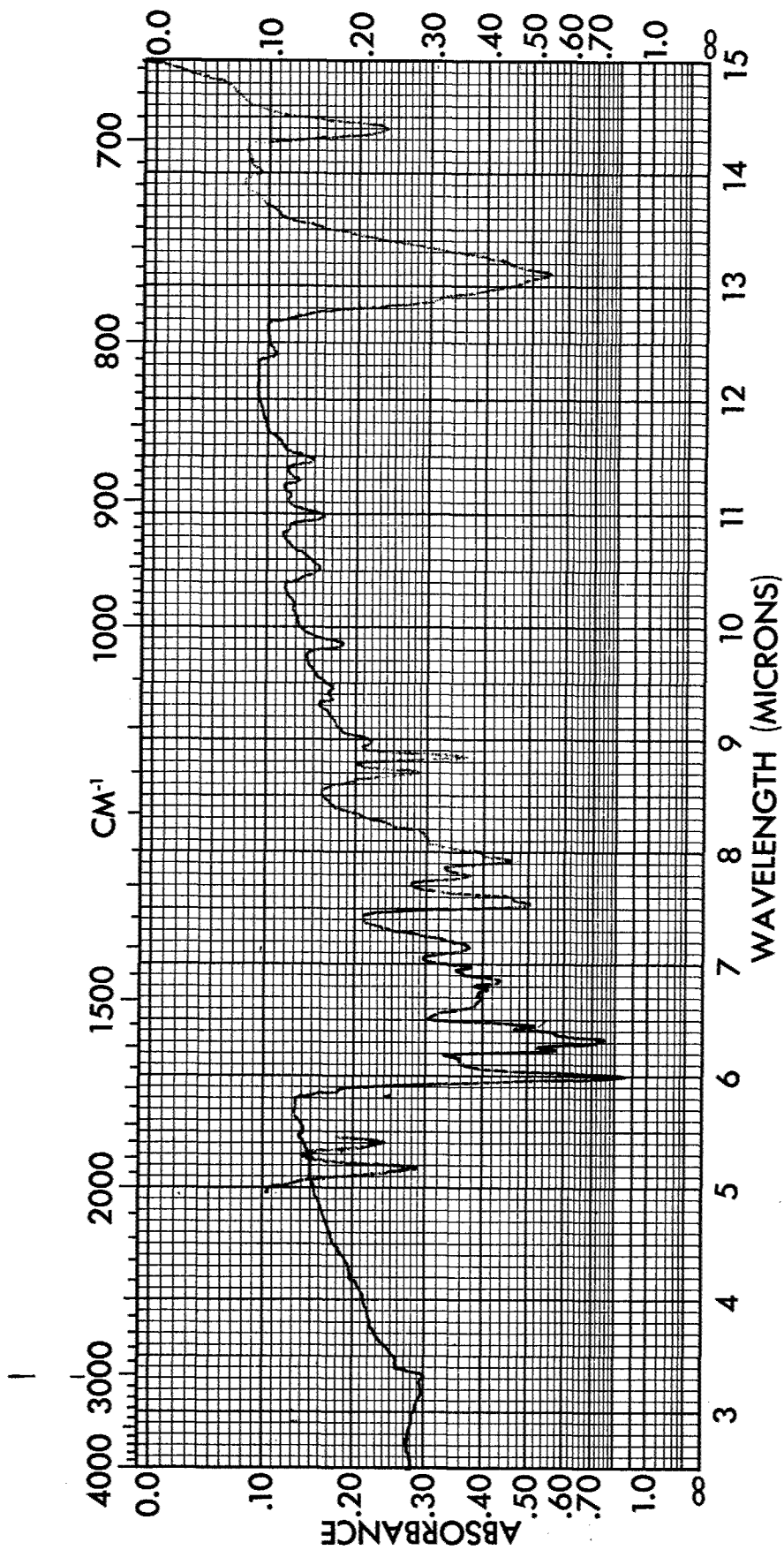


Figure 20. Infrared Spectrum of the Methanol-Insoluble Product 1-A1 (XVII) from the yellow sublimate 1-A

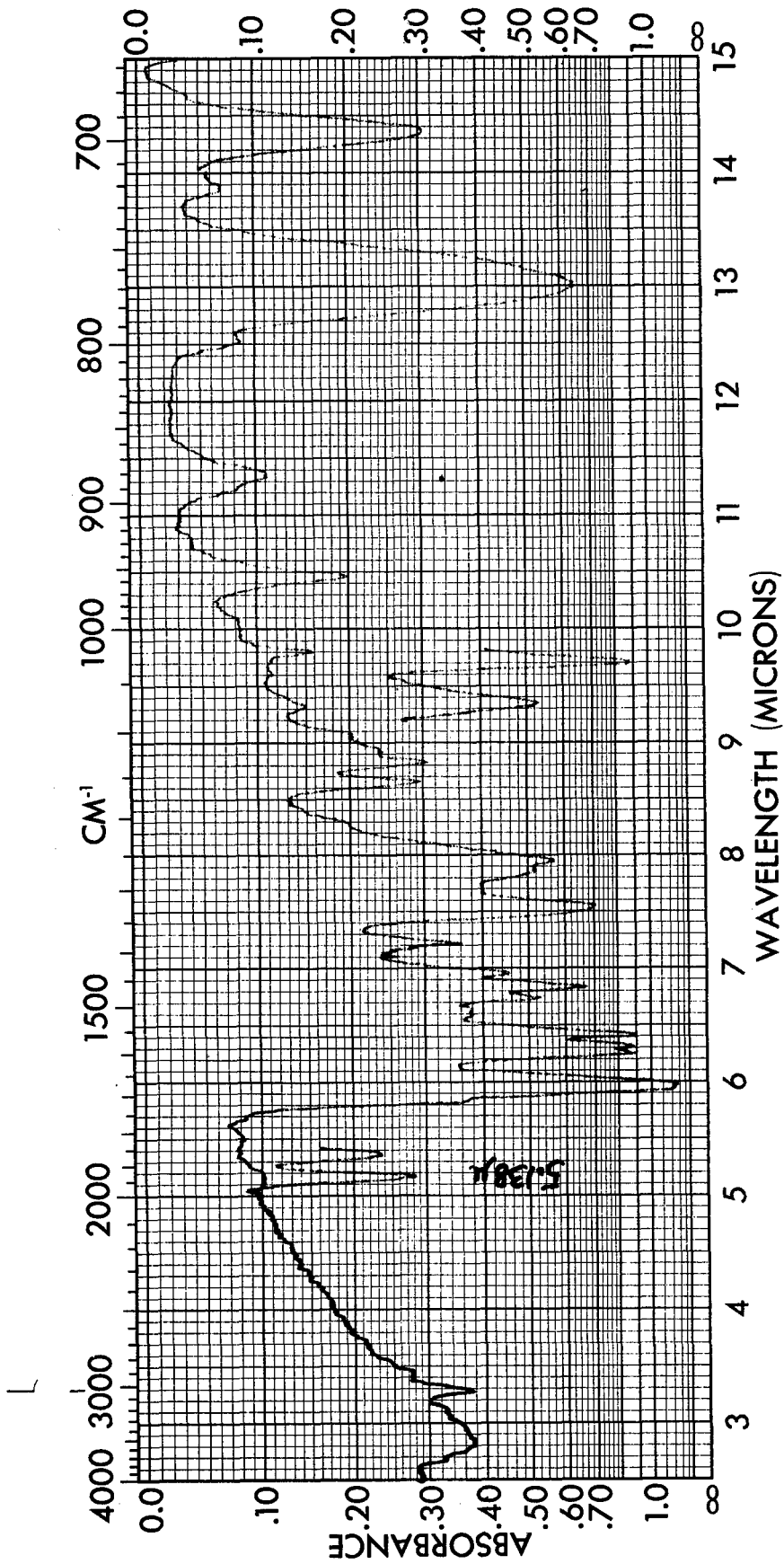


Figure 21. Infrared Spectrum of the Methanol-Insoluble Product 1-B1, After Extraction of the Residue, 1-B, in the Tube with Methanol

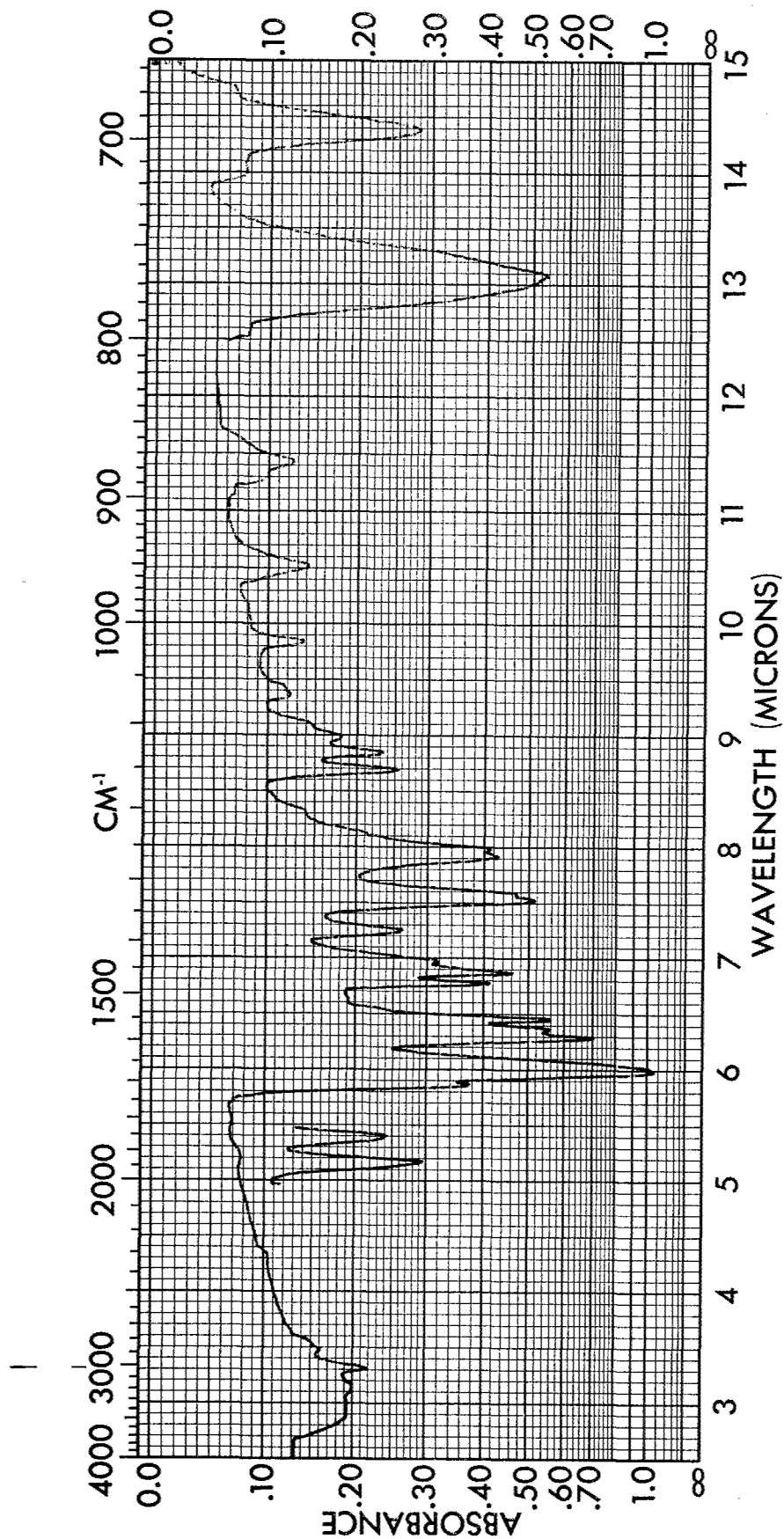


Figure 22. Infrared Spectrum of the Methanol-Soluble Product 1-B2 from Extraction of the Residue, 1-B, in the Tube with Methanol

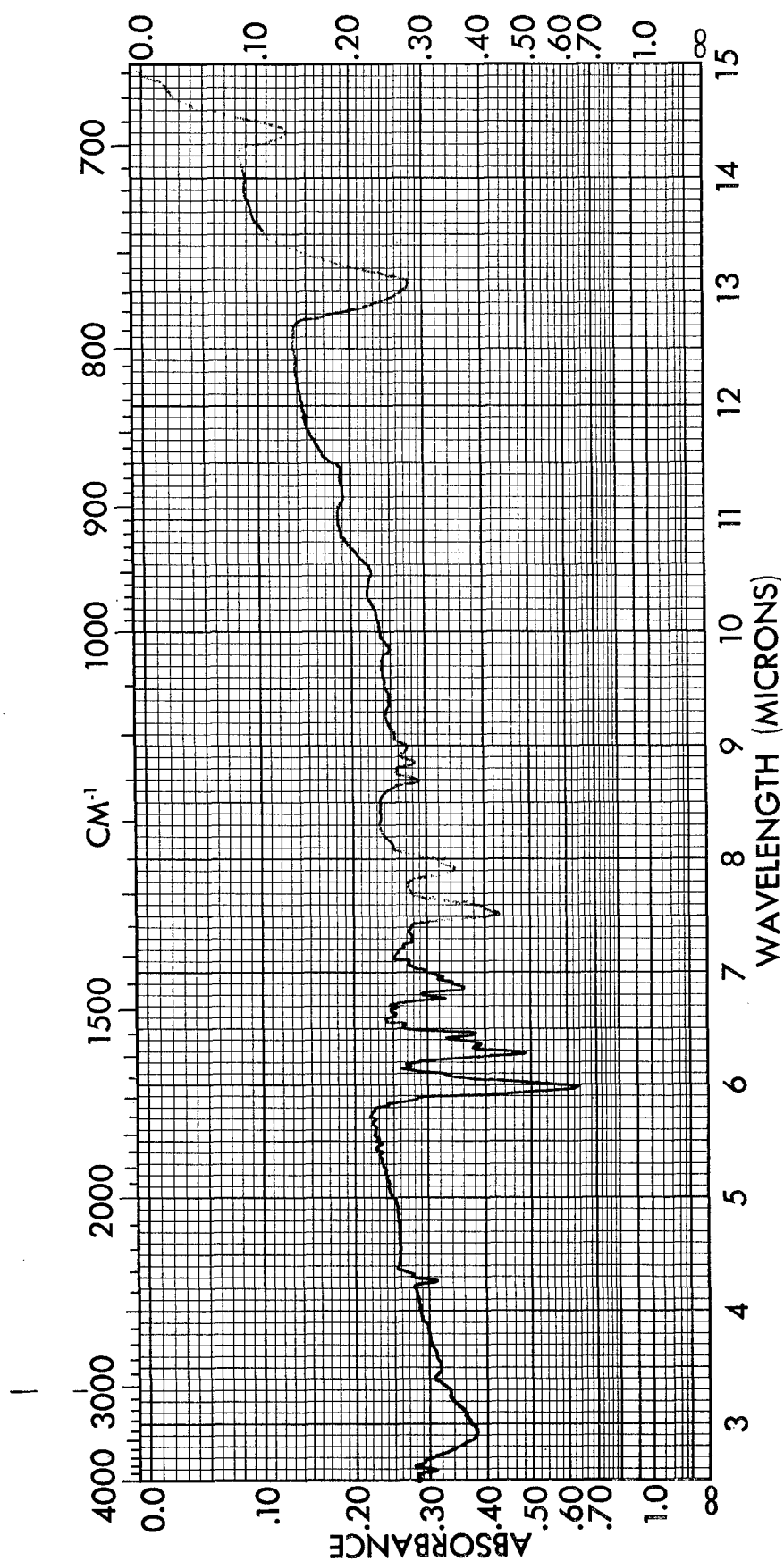


Figure 23. Infrared Spectrum of the Ether-Insoluble Product 1-B3 (impure XVII), mp 334-360°C from extraction of 1-B2

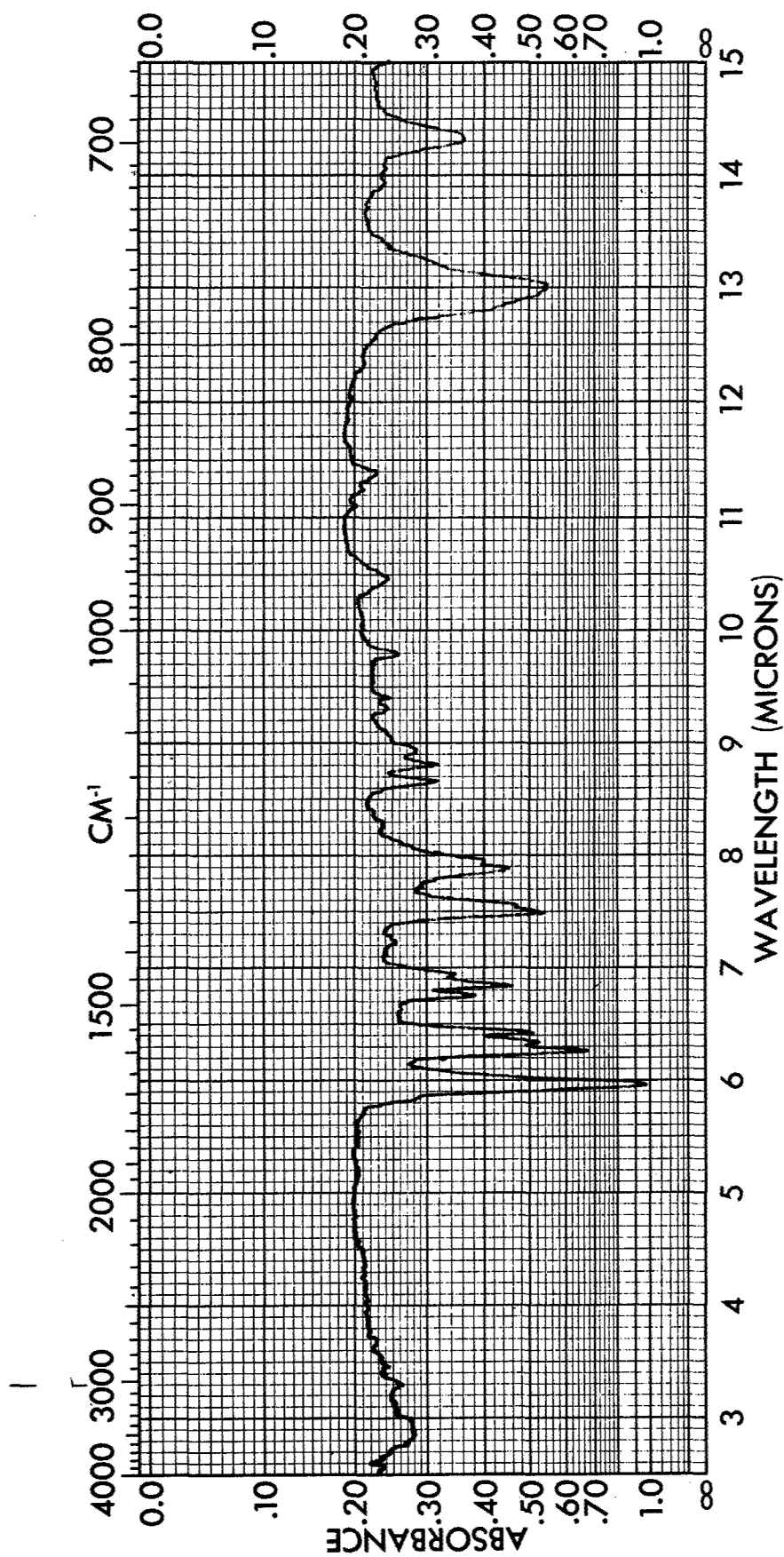


Figure 24. Infrared Spectrum of the Ethanol-Soluble Product 1-B4, XVII, mp 331-334°C, from 1-B3

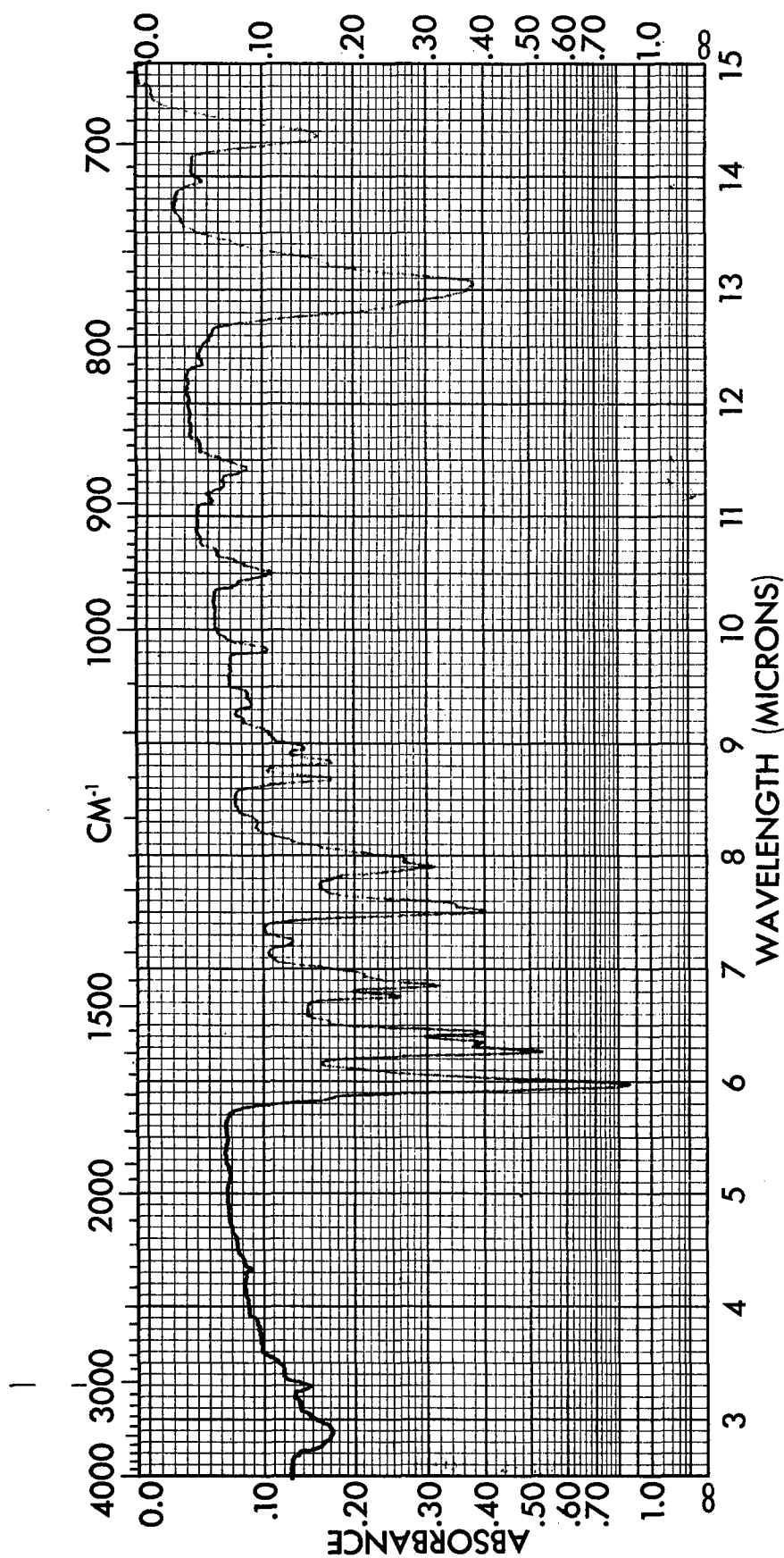


Figure 25. Infrared Spectrum of the Ethanol-Soluble Product 1-B5, XVII, mp 330-333°C

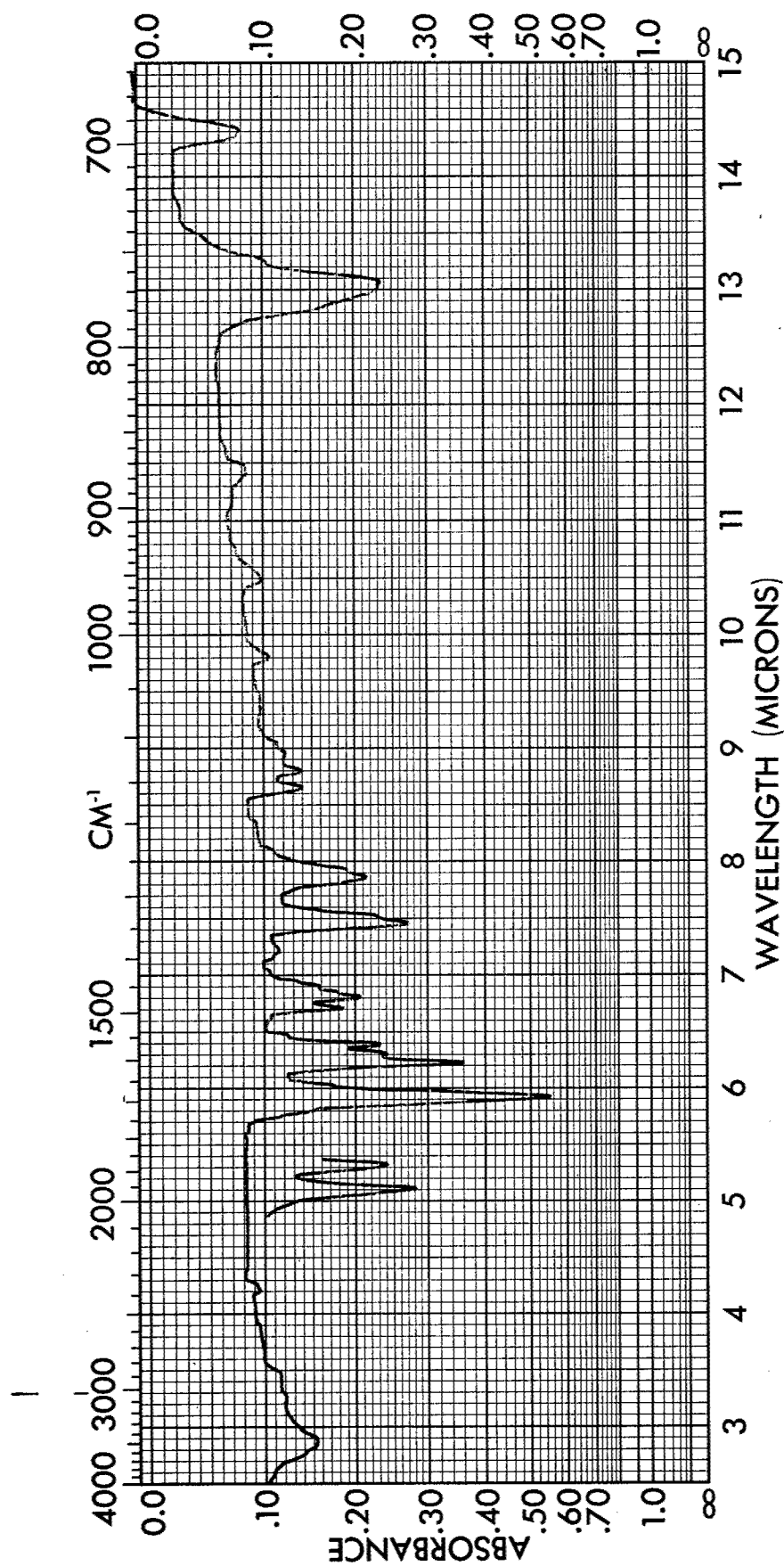


Figure 26. Infrared Spectrum of Ethanol-Soluble Product 1-B6, XVII
mp > 360°C

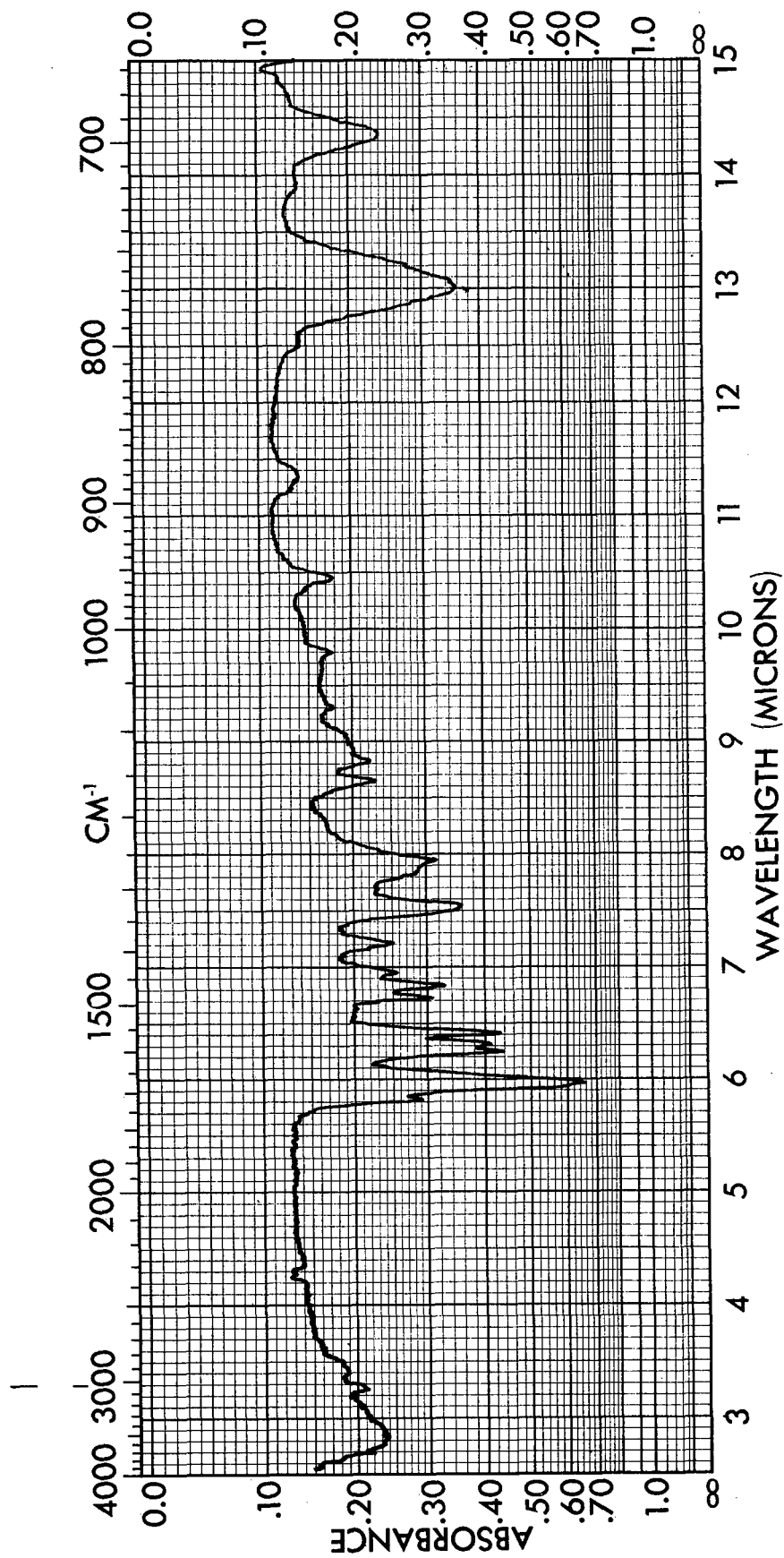


Figure 27. Infrared Spectrum of Product 1-C1, XVIII, mp 251-253°C

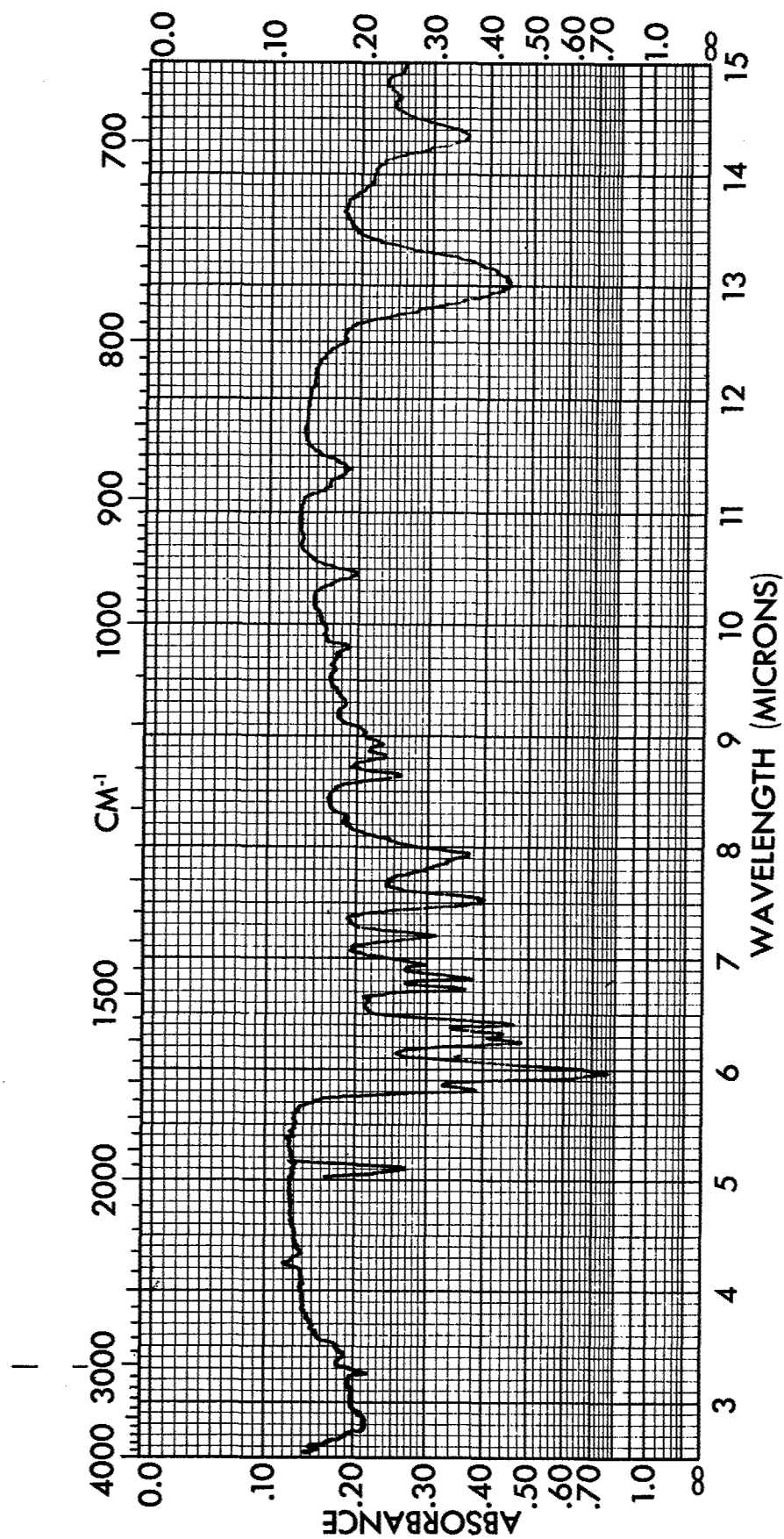


Figure 28. Infrared Spectrum of Product 1-C2, XVIII, mp 248-251°C

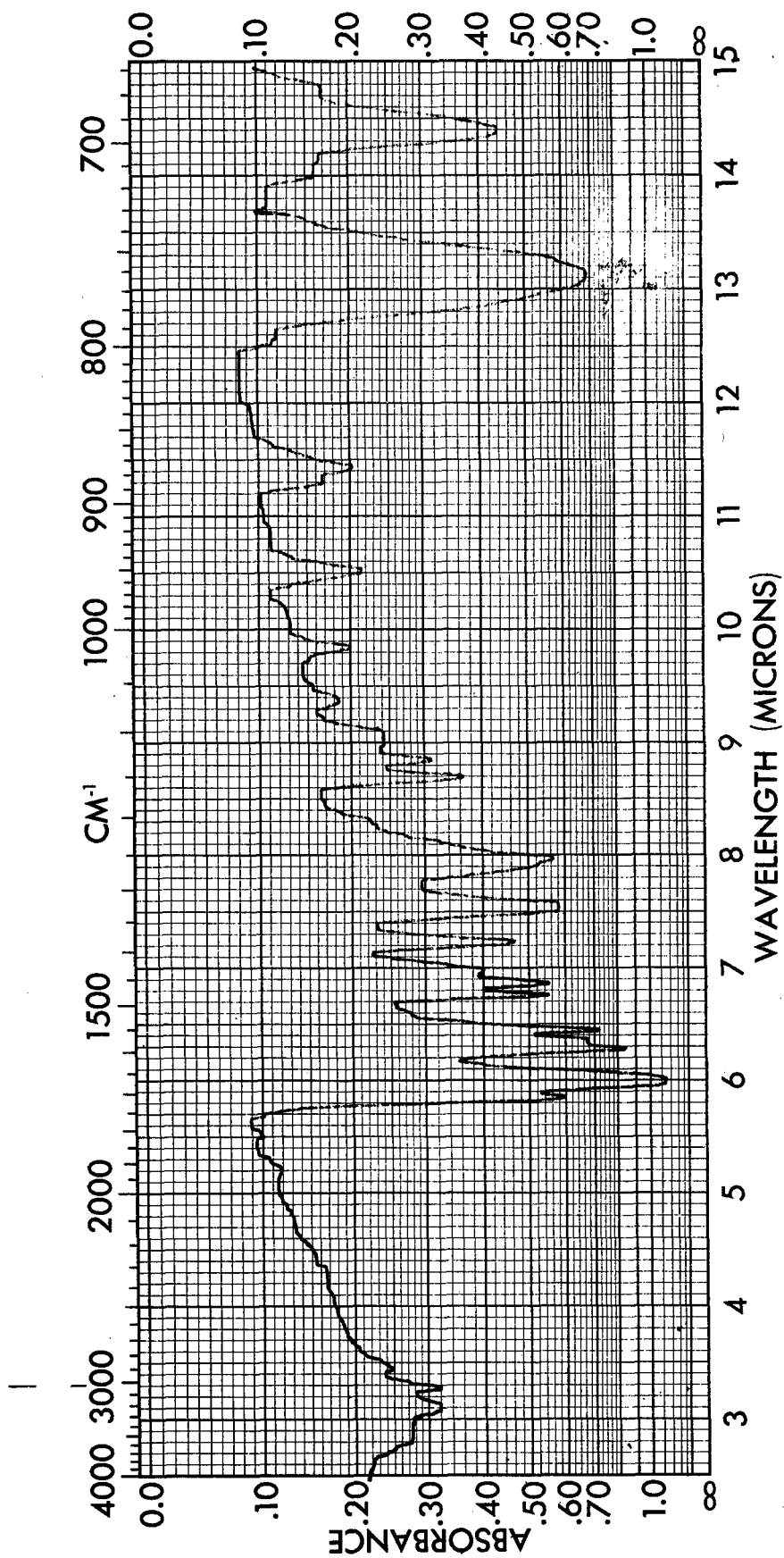


Figure 29. Infrared Spectrum of Product 1-C3, XVIII, mp 244-249°C

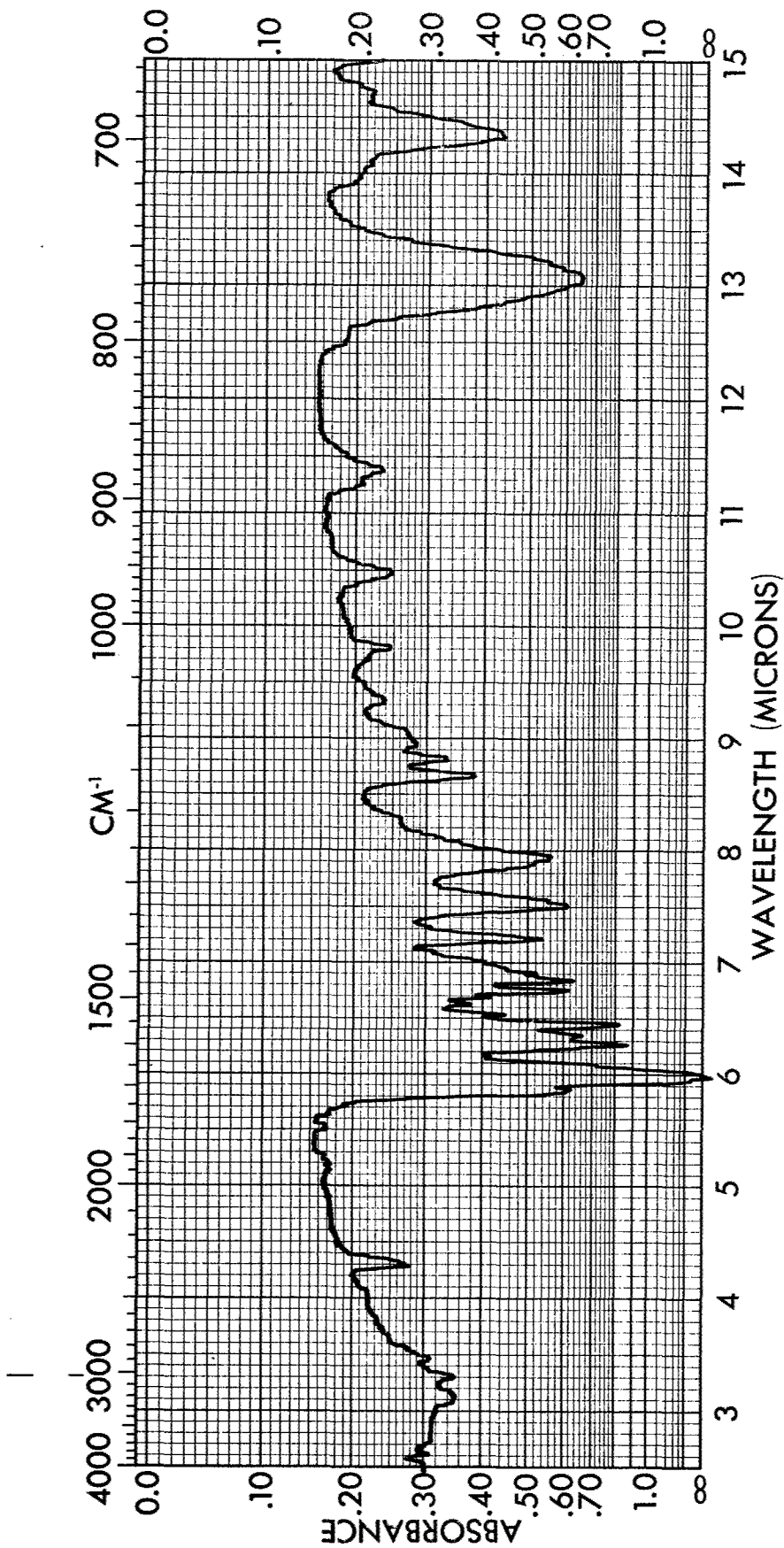


Figure 30. Infrared Spectrum of Product 1-C4, XVIII, mp 230-235°C

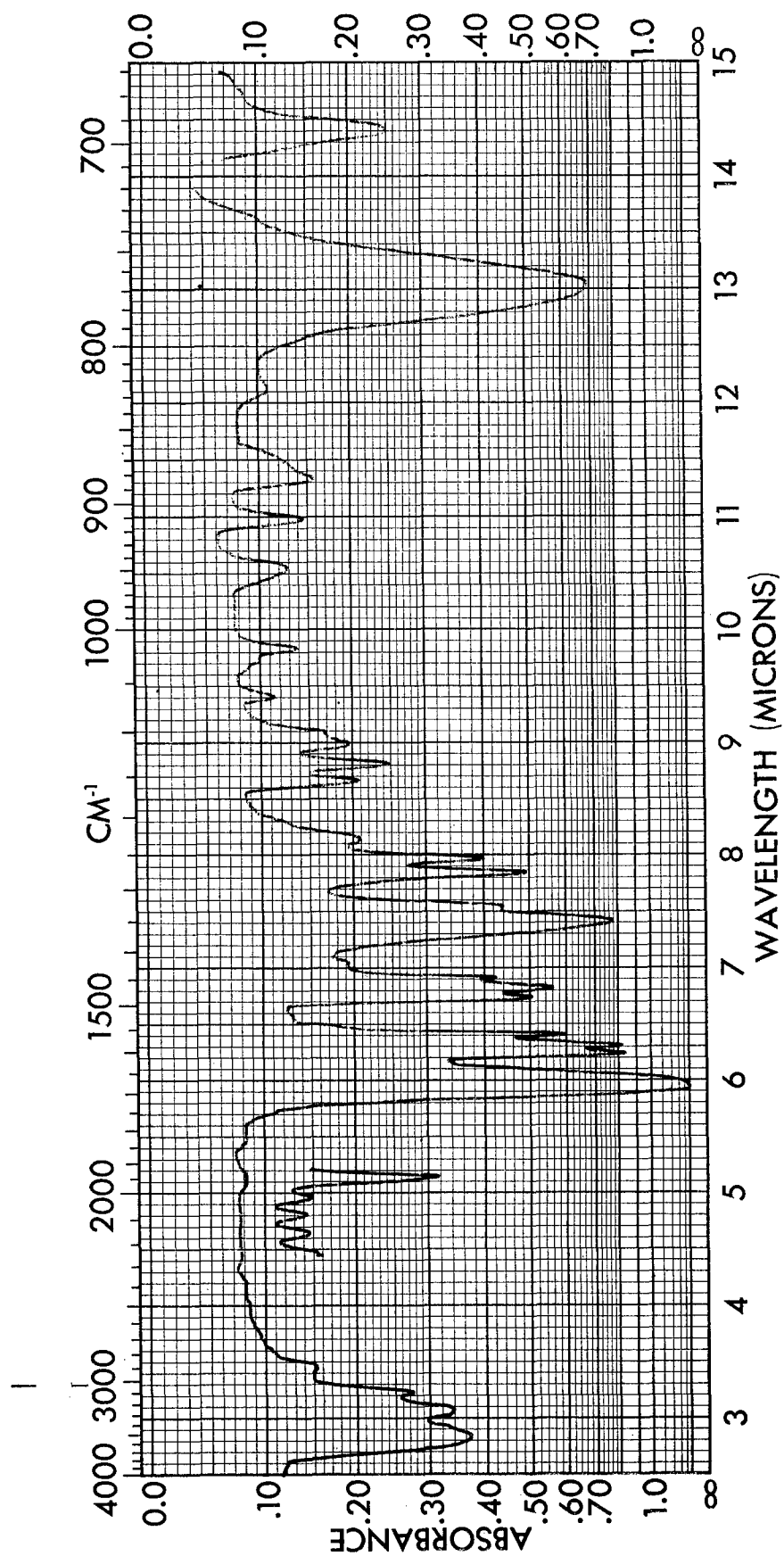


Figure 31. Infrared Spectrum of the Benzene-Insoluble Product 2-Al, XVII, from Thermal Decomposition of [4H], 3, l-benzoxazine-2,4, [1H]-dione, XV

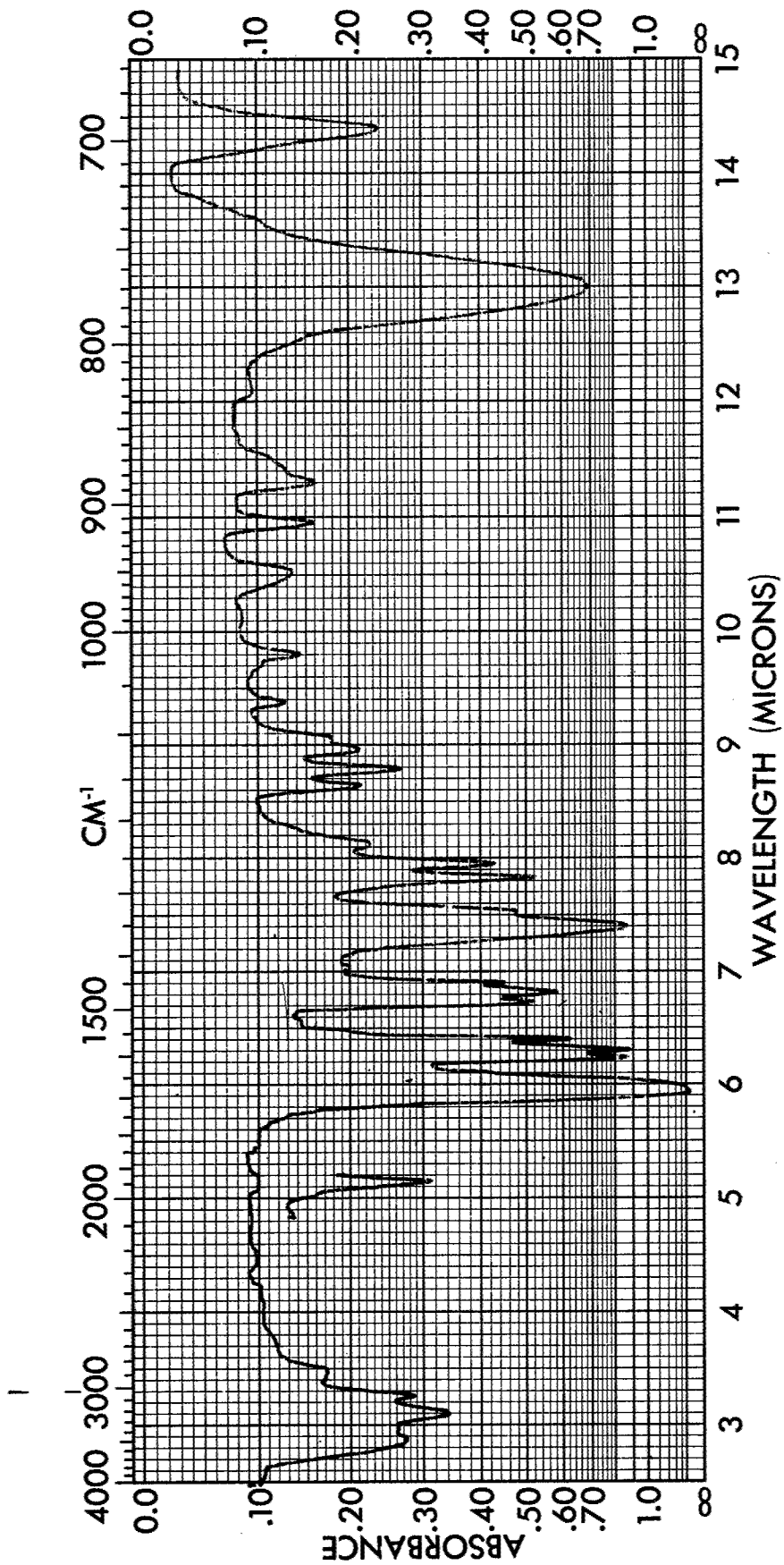


Figure 32. Infrared Spectrum of the Yellow Sublimate 2-AIA, XVII,
mp 300-302°C

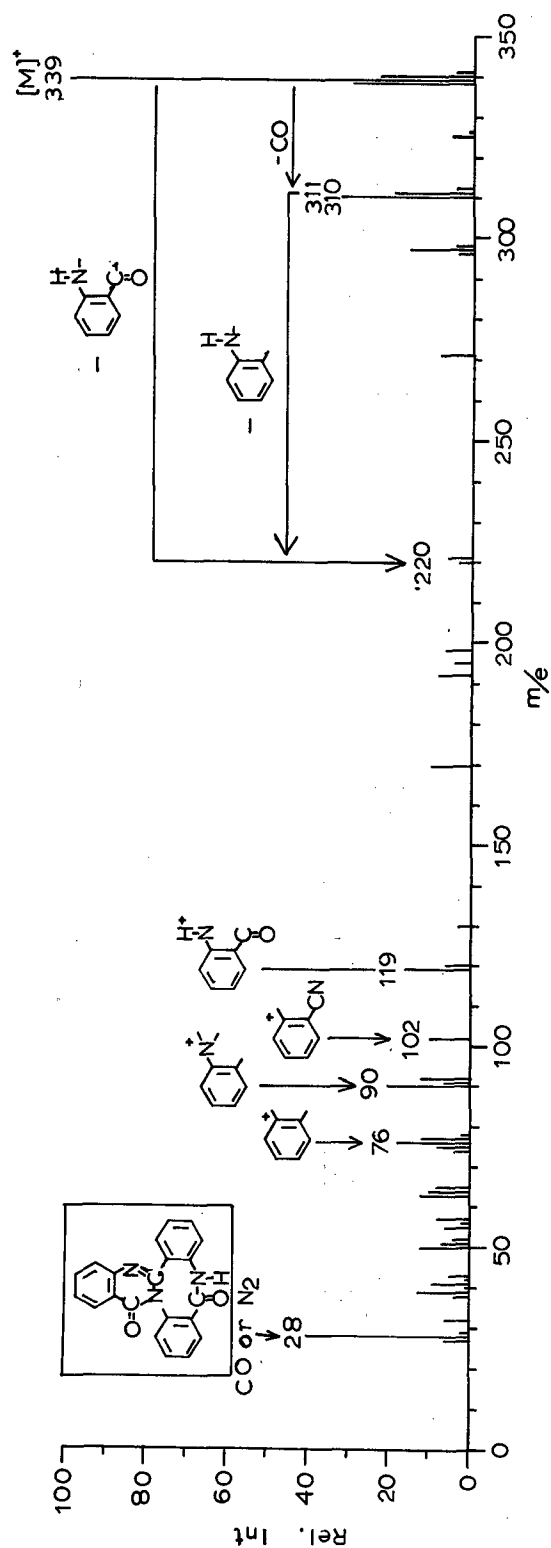


Figure 33. Mass Spectrum of the Yellow Sublimate 2A1A, XVII, mp 300-302°C

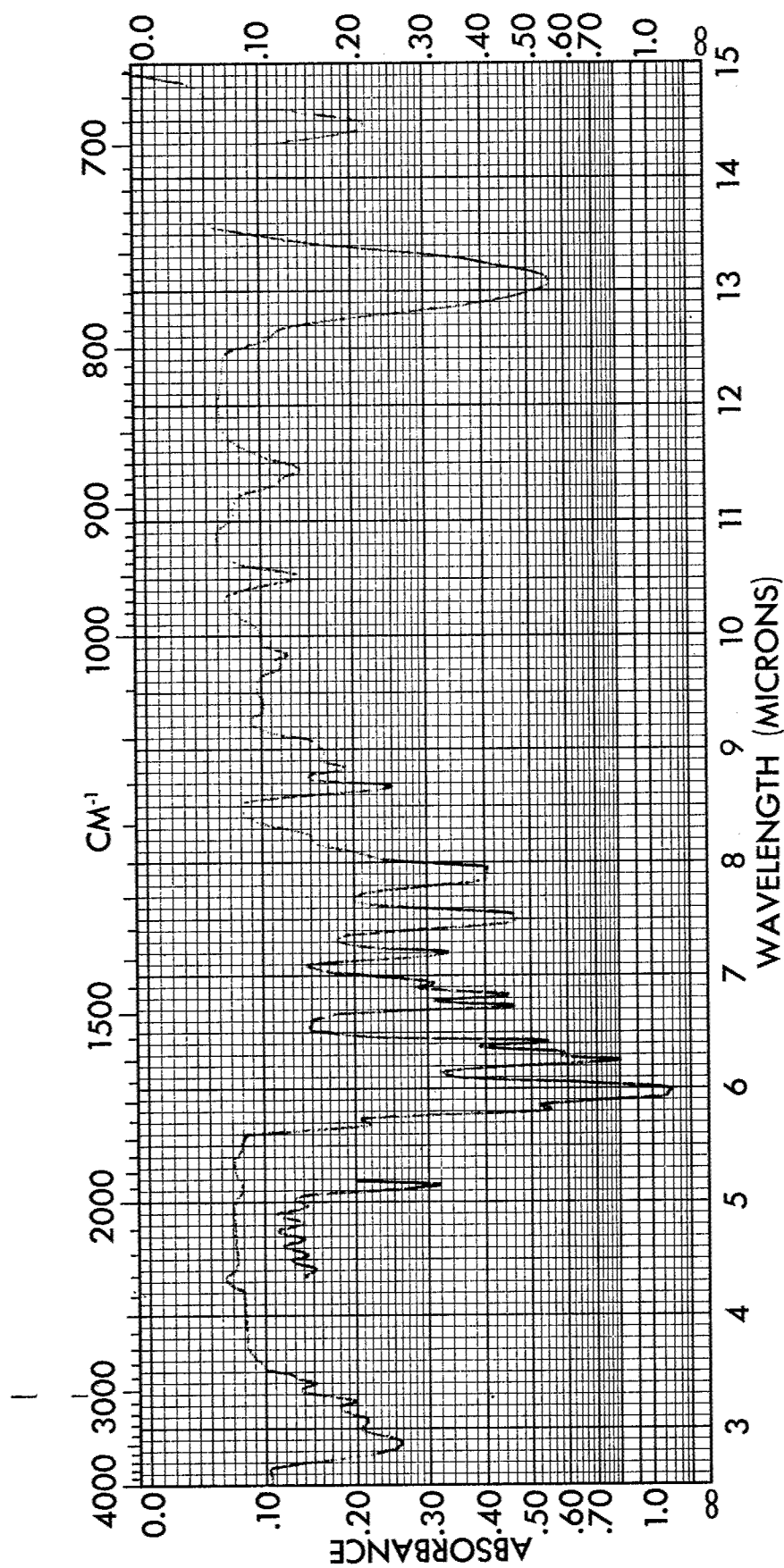


Figure 34. Infrared Spectrum of the Benzene-Soluble Product 2-A3 from Thermal Decomposition of [4H], 3,1-benzoxazine-2,4, [1H]-dione, XV, mp 225-230°C

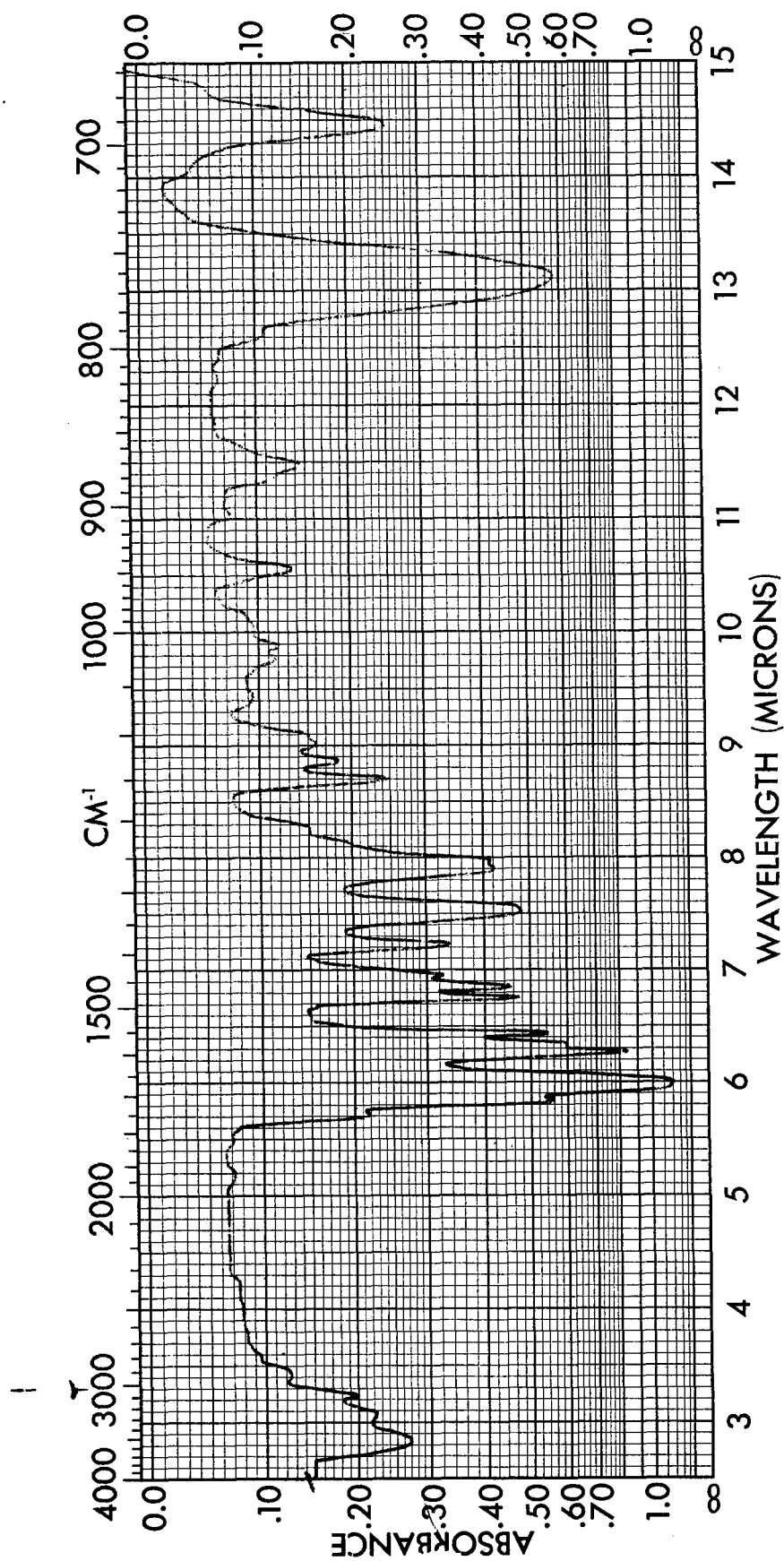


Figure 35. Infrared Spectrum of the Yellow Sublimate 2-A4, XIX,
mp 210-215°C

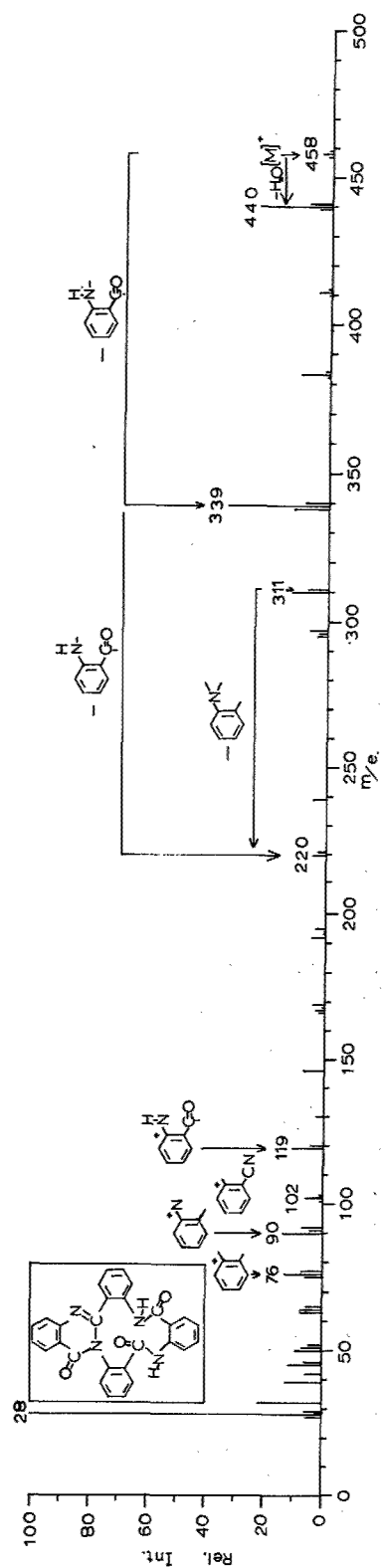


Figure 36. Mass Spectrum of the Yellow Sublimate 2-A4, XIX, mp 210-215°C

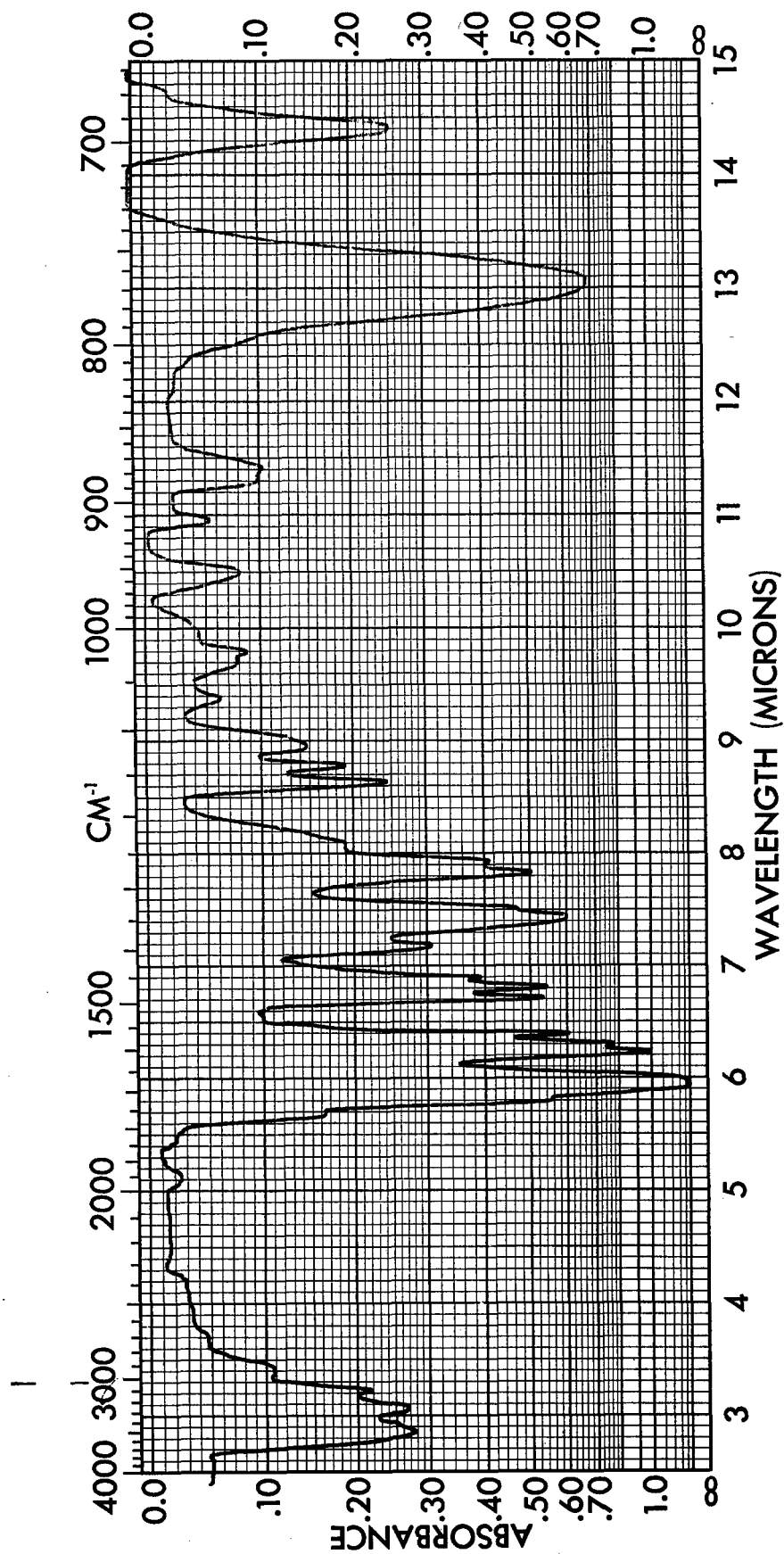


Figure 37. Infrared Spectrum of the Yellow Sublimate 2-A5, XIX,
mp 212-218°C

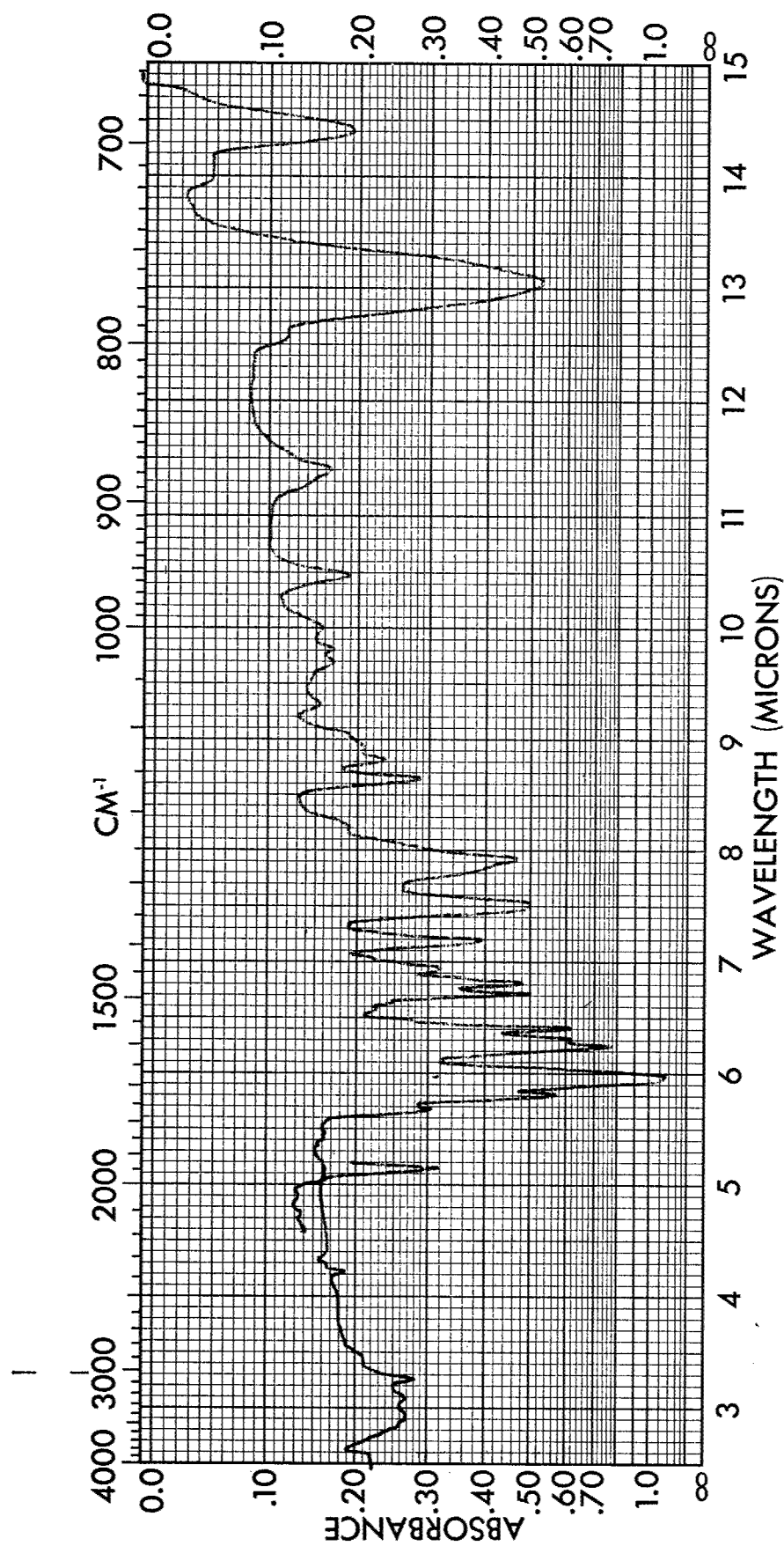


Figure 38. Infrared Spectrum of Unsublimed 2-A5A, XIX, mp 235-250°C

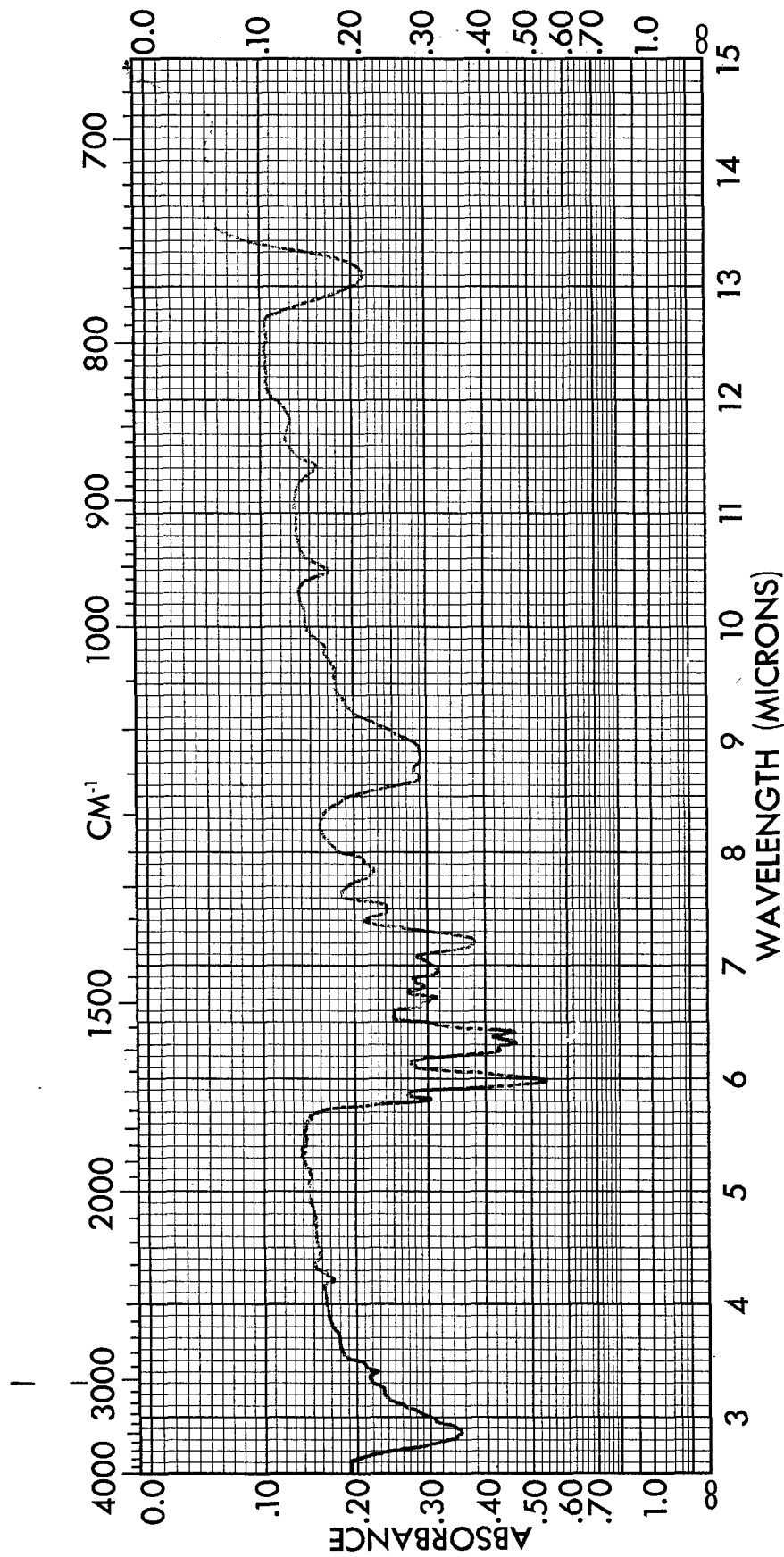


Figure 39. Infrared Spectrum of Product 2-A3A from Chromatogram of Product 2-A3

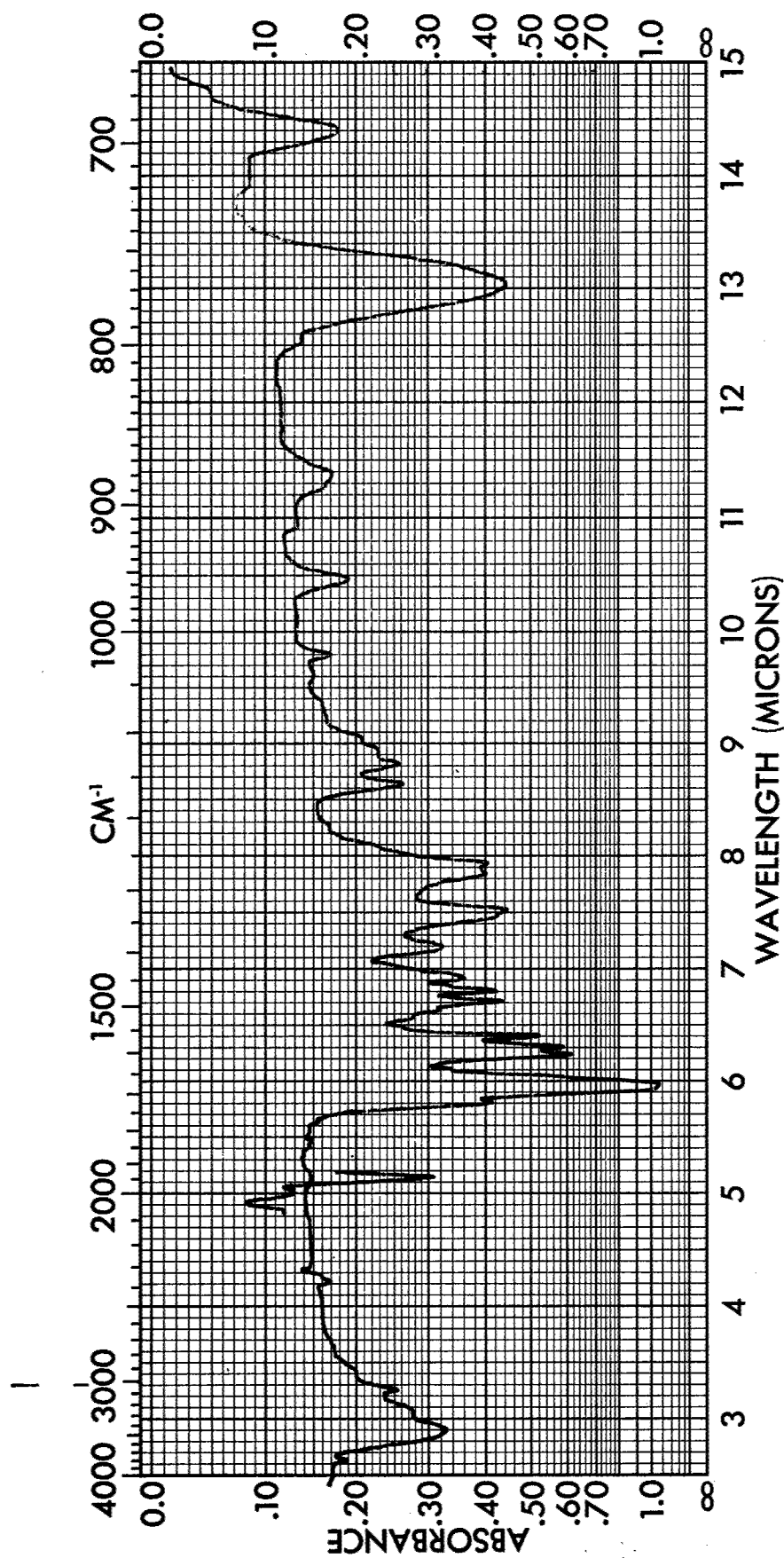


Figure 40. Infrared Spectrum of Product 2-A3B, XVIII, from Chromatogram of Product 2-A3

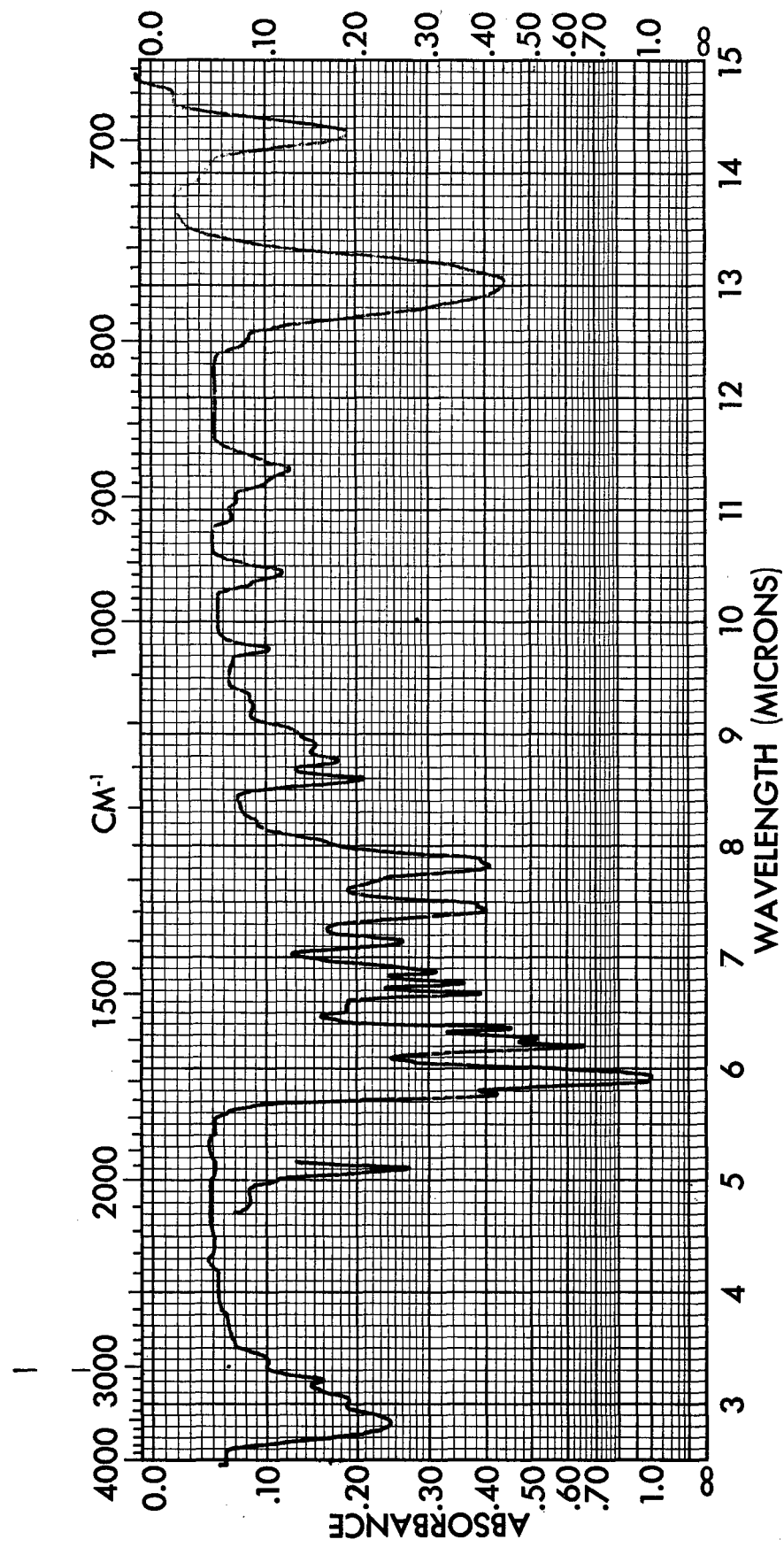


Figure 41. Infrared Spectrum of Product 2-A3C, XVIII, from Chromatogram of Product 2-A3

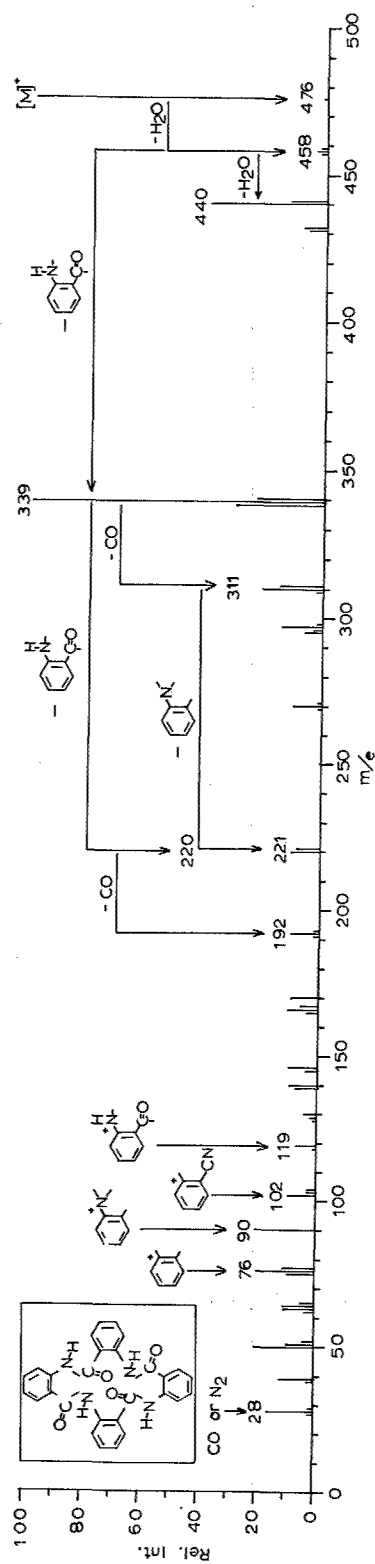


Figure 42. Mass Spectrum of Product 2-A3C, XVIII, from Chromatogram of Product 2-A3

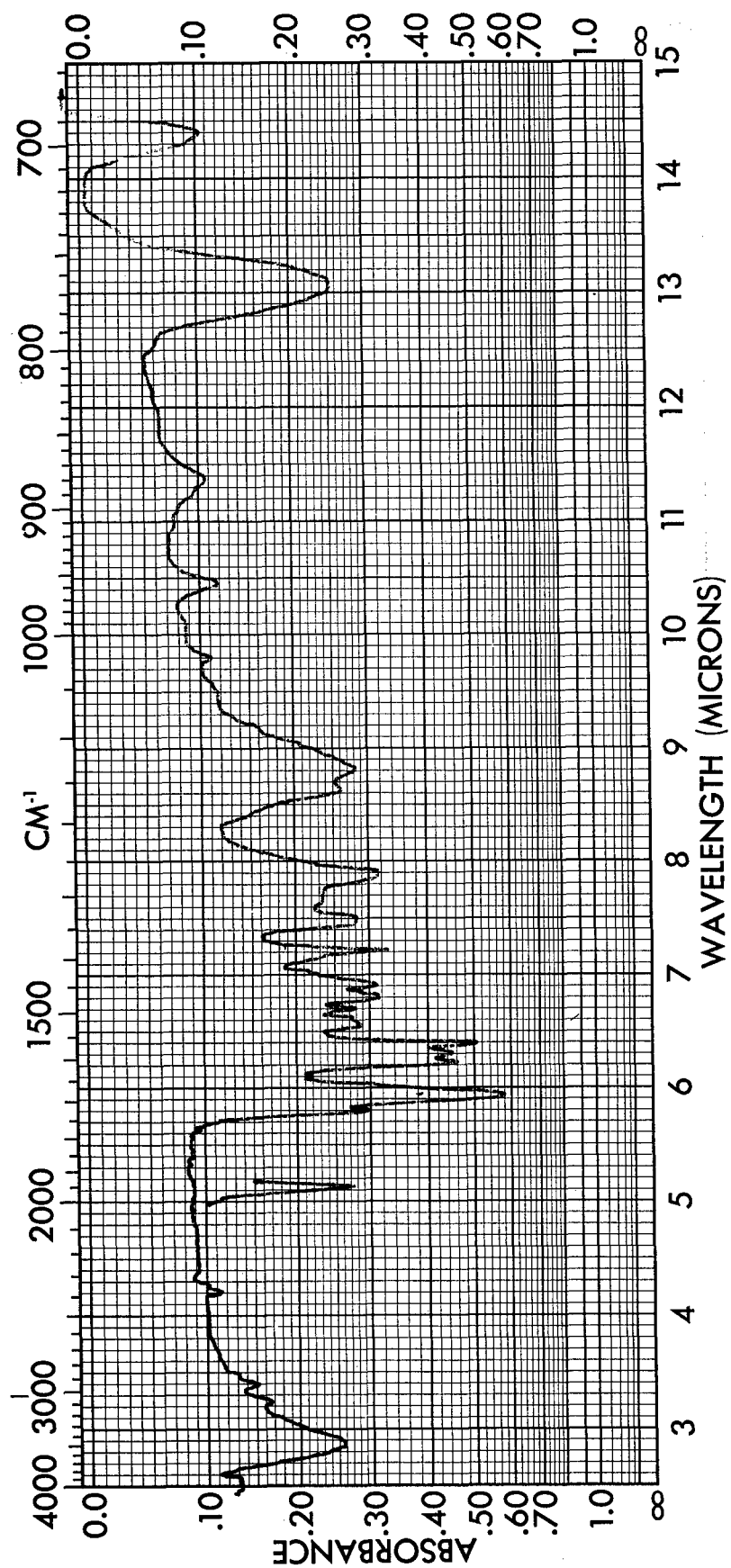


Figure 43. Infrared Spectrum of Product 2-A3D from Chromatogram of Product 2-A3

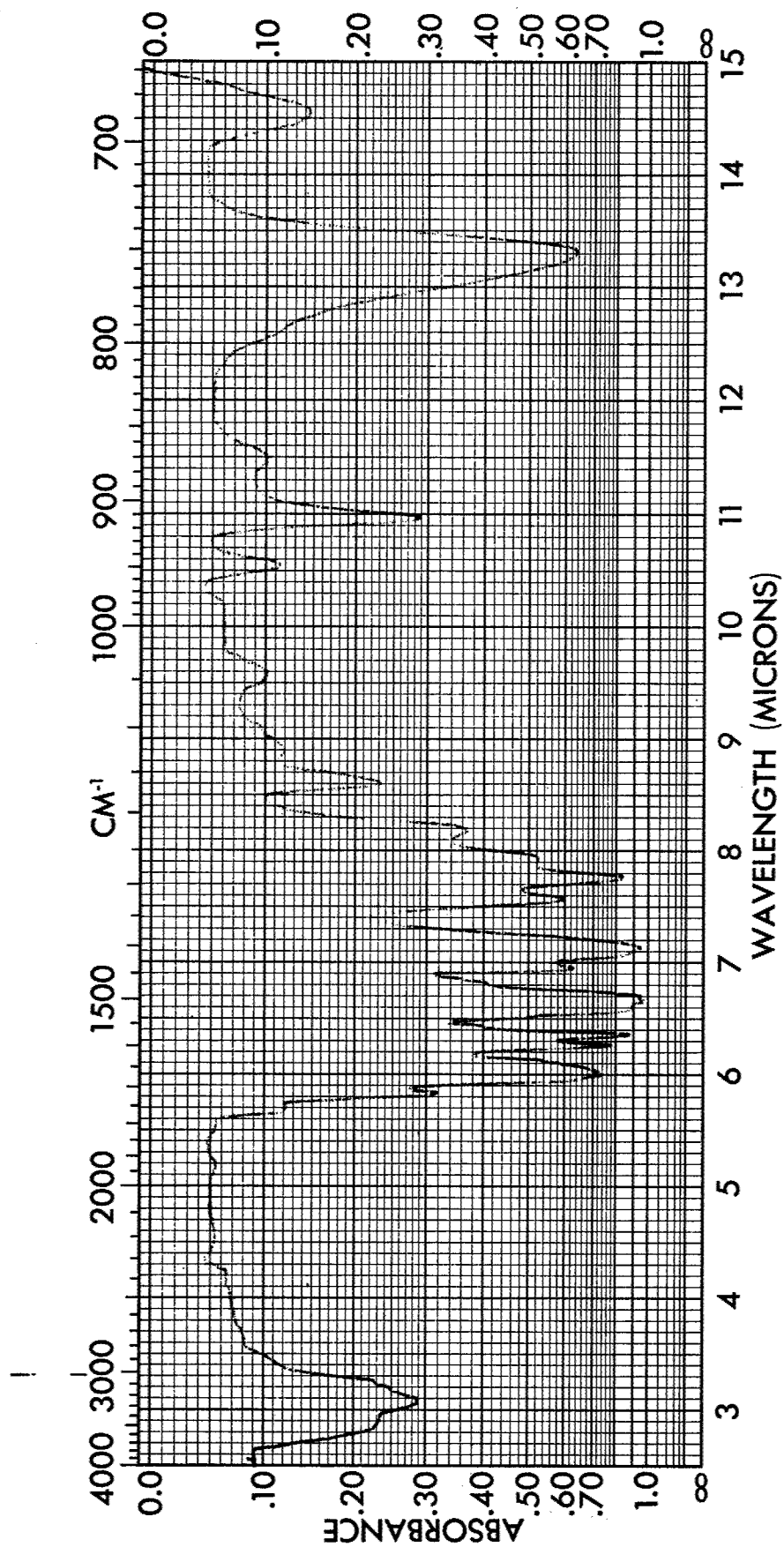


Figure 44. Infrared Spectrum of Benzene-Insoluble Product 2-B1, XX

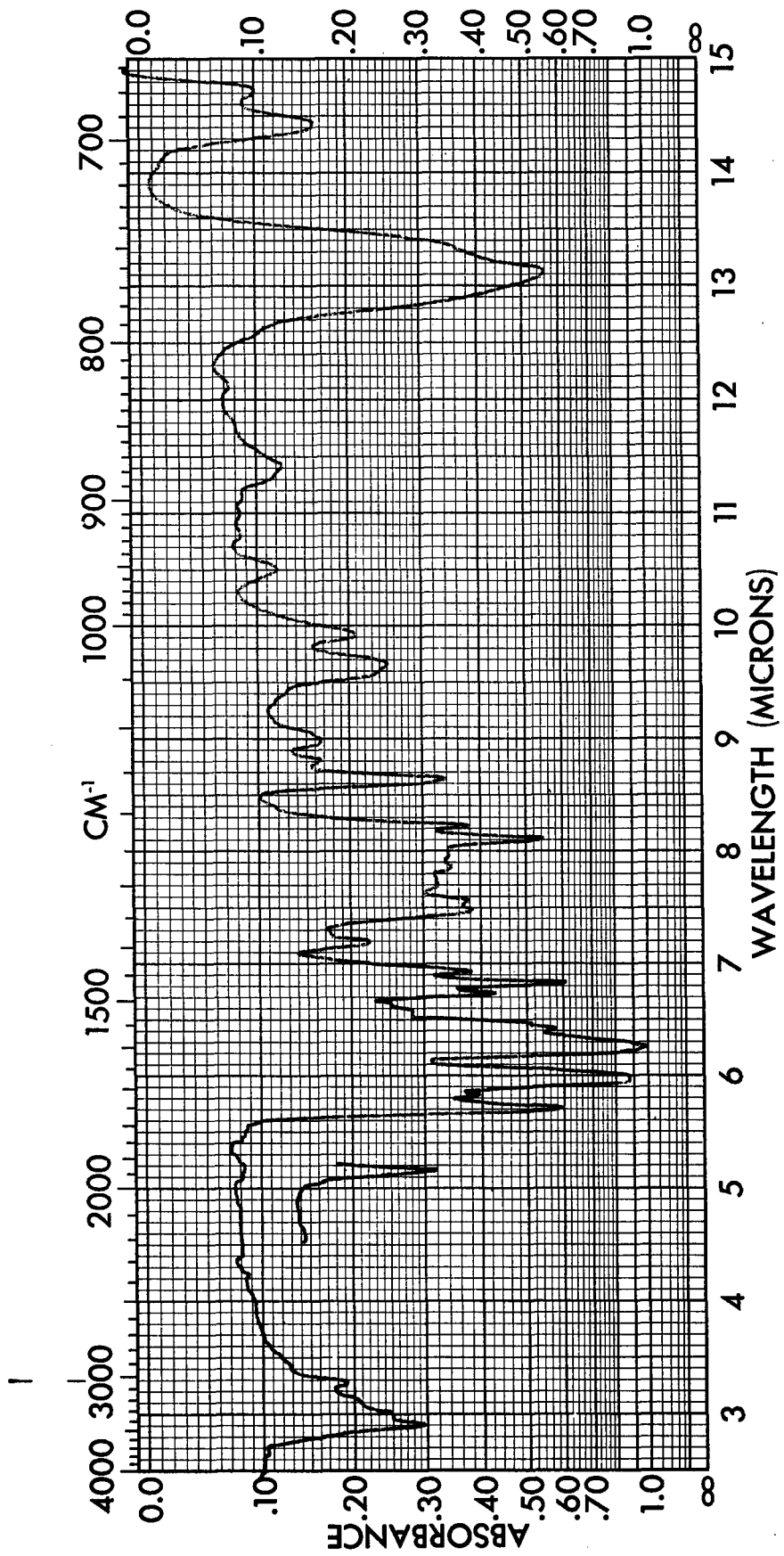


Figure 45. Infrared Spectrum of the Yellow Sublimate 2-81A, X

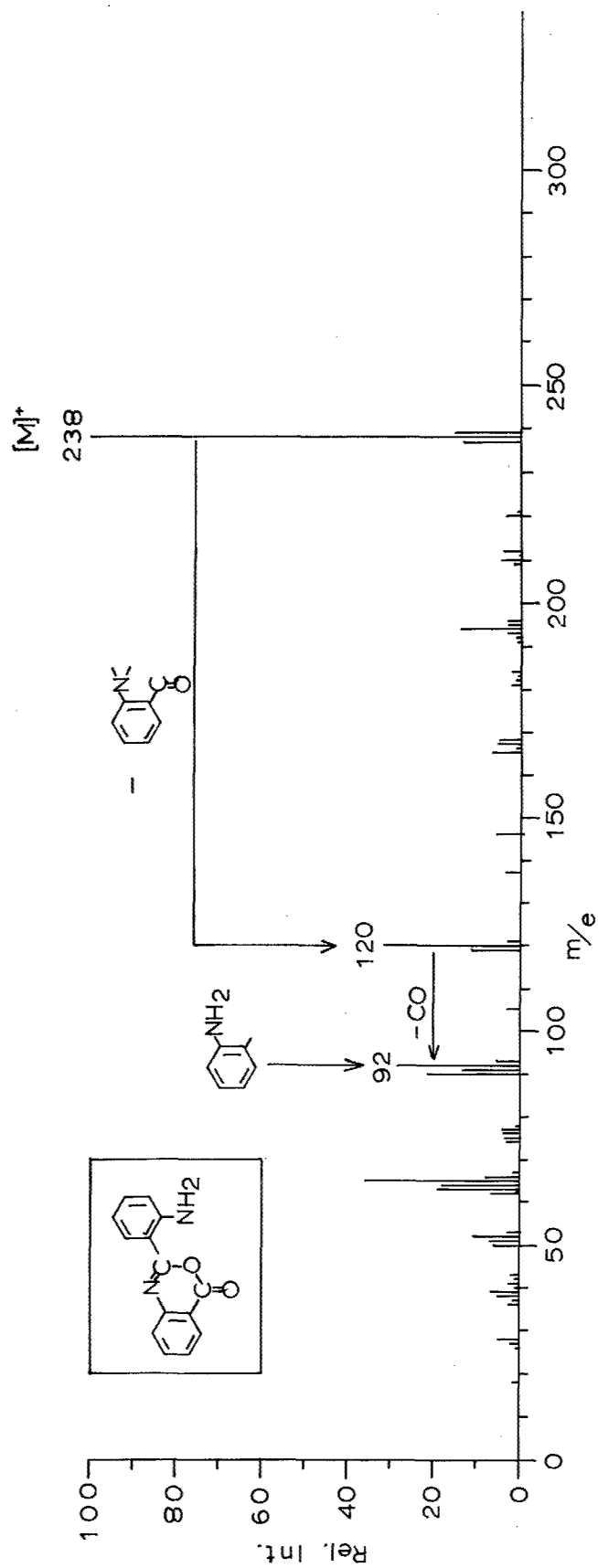


Figure 46. Mass Spectrum of the Yellow Sublimate 2-B1A, X

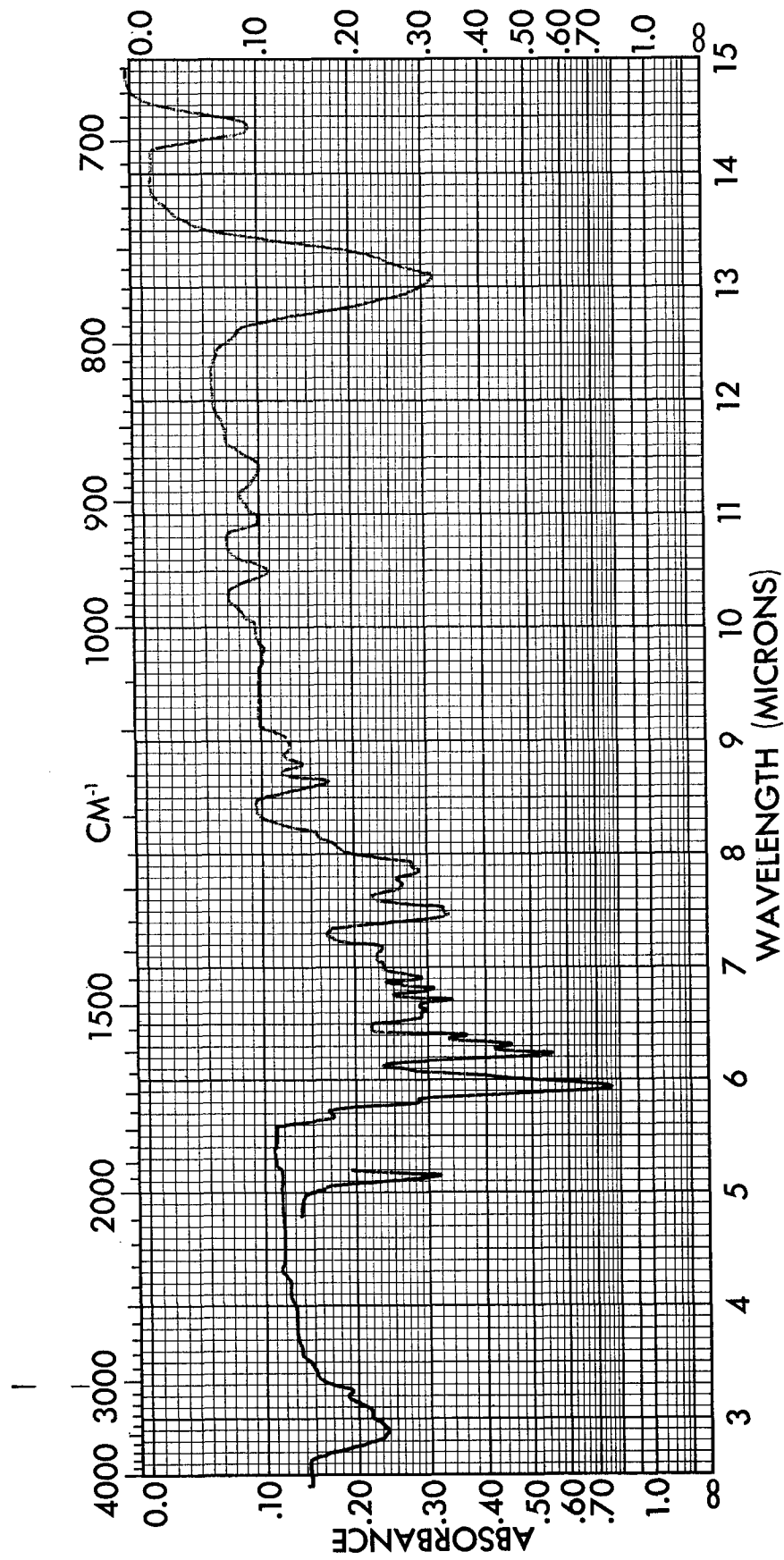


Figure 47. Infrared Spectrum of Product 2-B1B, XX, after Heating 2-B1A at 250°C under Nitrogen

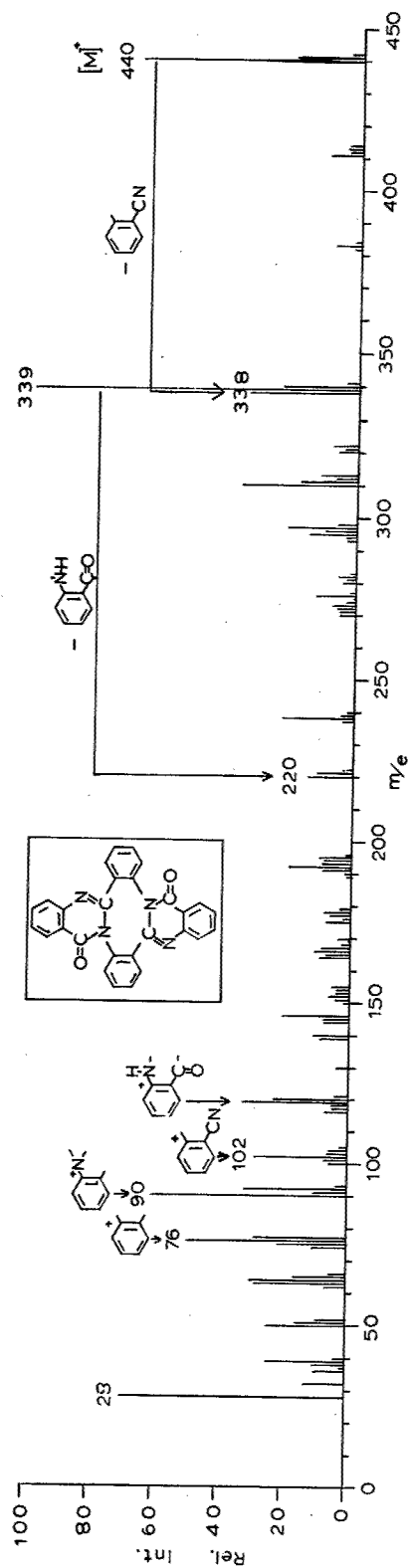


Figure 48. Mass Spectrum of Product 2-B1B, i.e., 10H, 21H-dibenzo-[3,4; 7,8][1,5]-diazocino-[2,1-b; 6,5-b']-diquinazoline-10, 21-dione, XX, after Heating 2-B1A at 250°C under Nitrogen

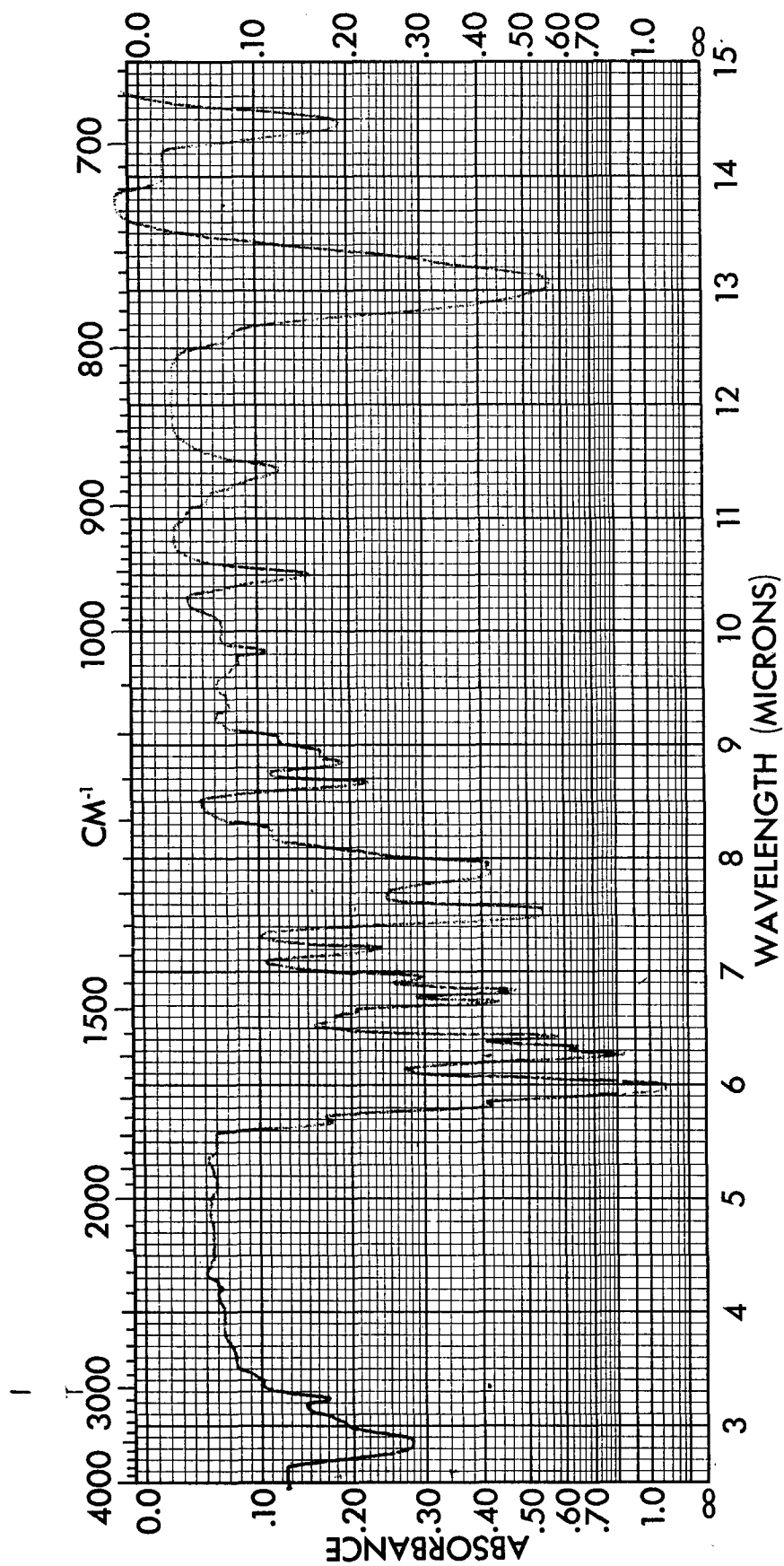


Figure 49. Infrared Spectrum of Benzene-Soluble Product 2-B2, XX, mp 295-300°C

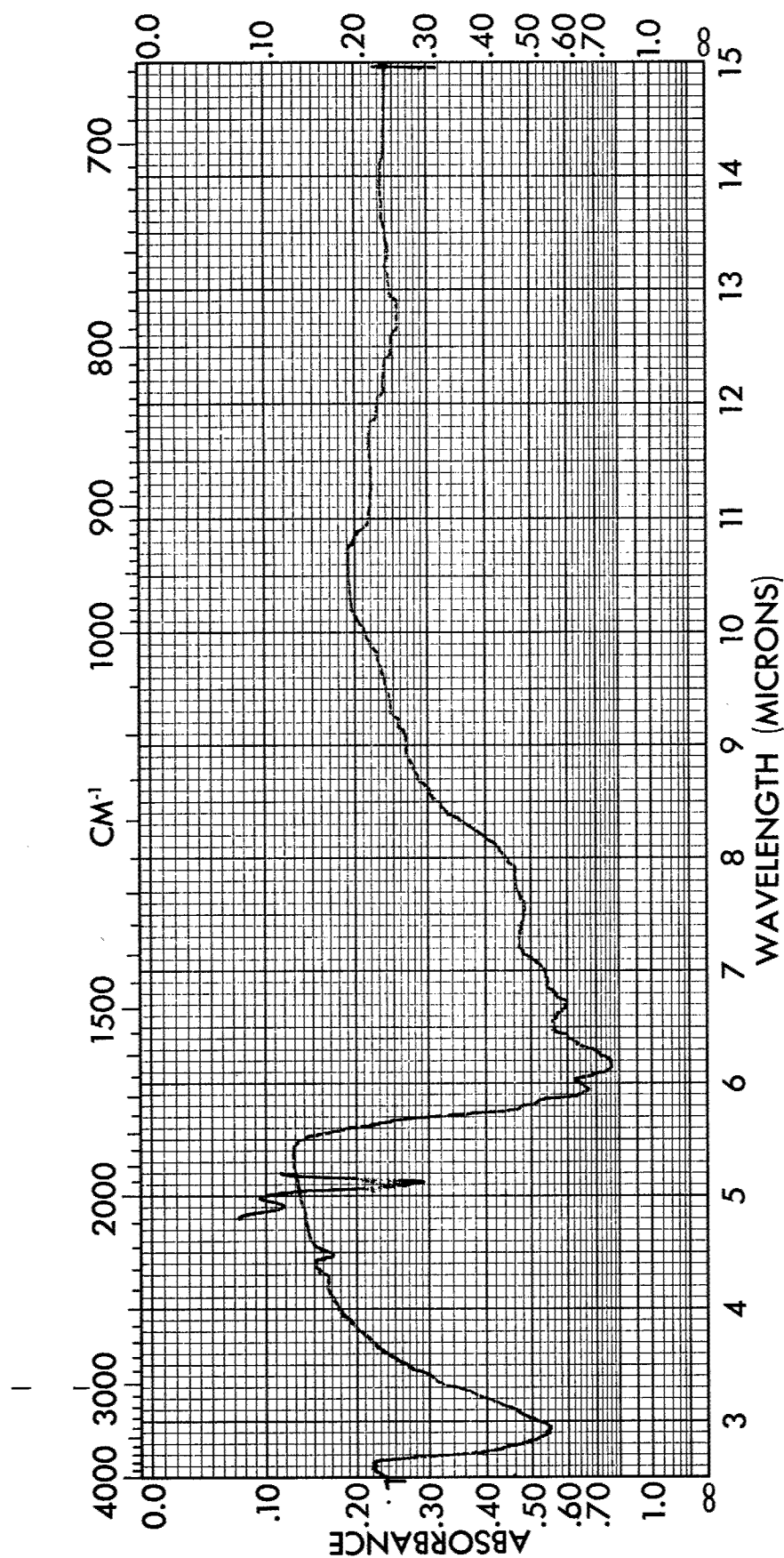


Figure 50. Infrared Spectrum of the Polymer $C_{32}H_{14}O_7Ng$, XL, from Thermal Decomposition of $[2H,7H], 3,1,8,6$ -benzobisoxazine-2,4,7,9, $[1H,6H]$ -tetraone, XXVI, at 360°C under Nitrogen (Run No. 1)

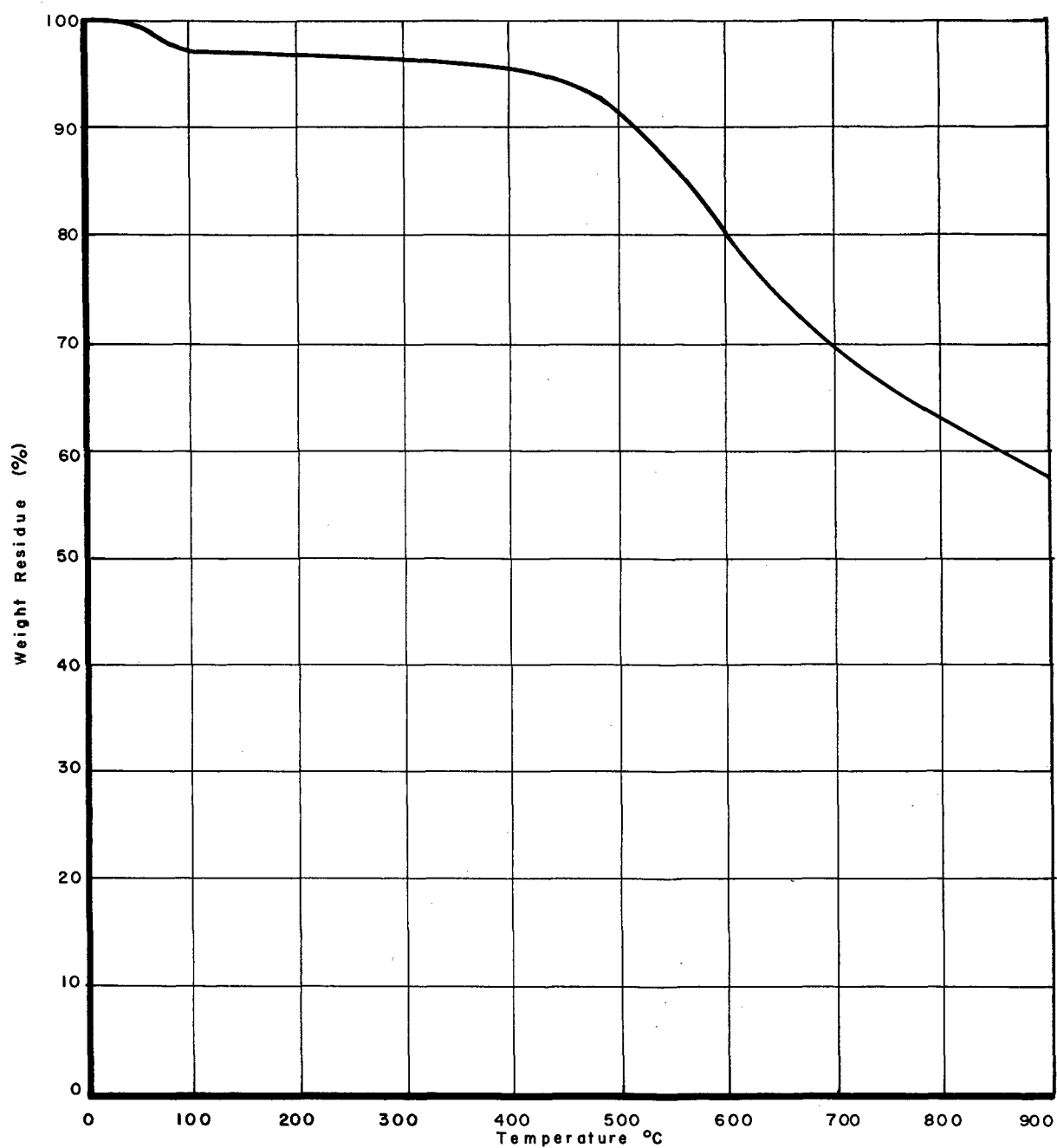


Figure 51. TGA Curve of the Polymer $C_{32}H_{14}O_7N_8$, XL, from Thermal Decomposition of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXVI, at 360°C under Nitrogen (Run No.1)

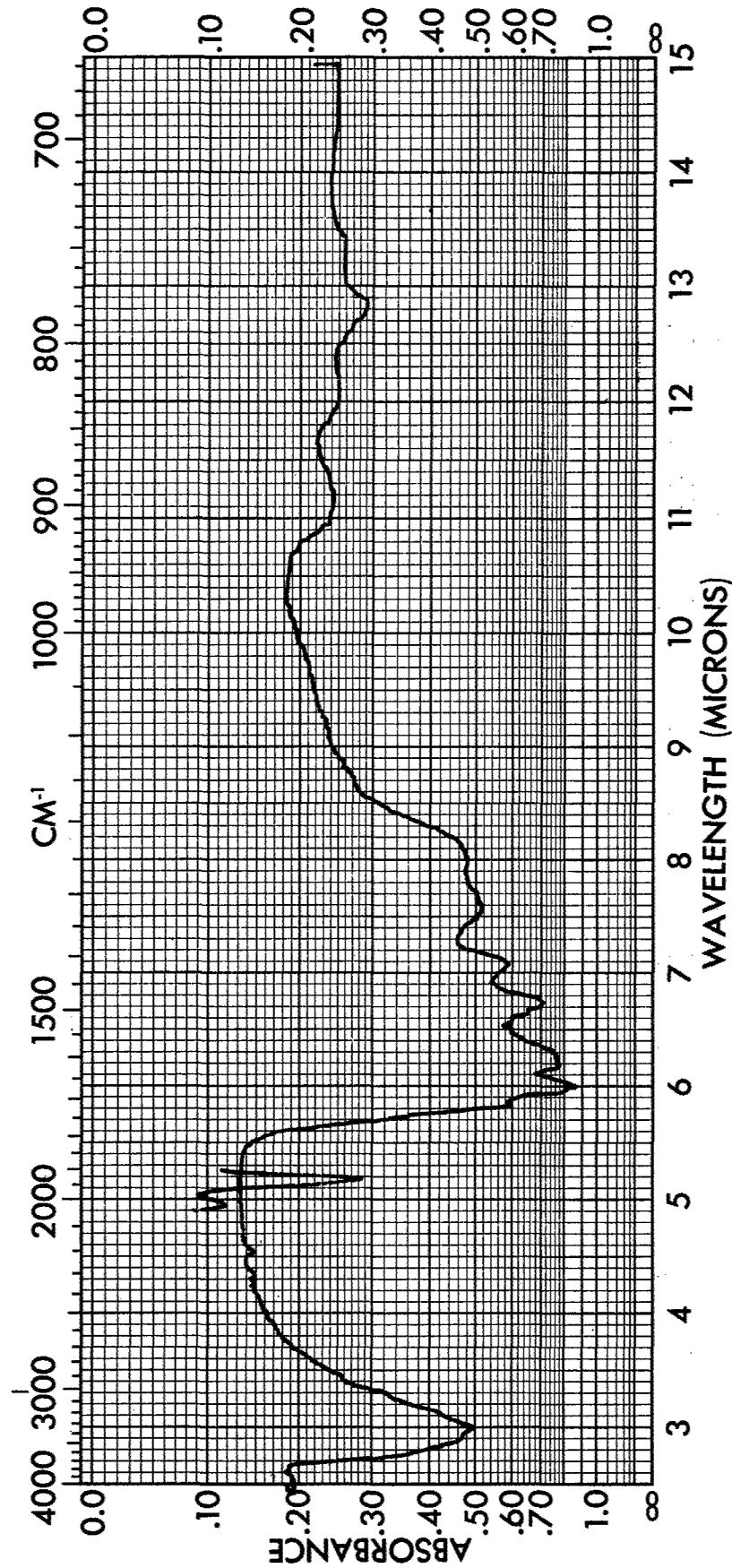


Figure 52. Infrared Spectrum of the Polymer $C_{32}H_{12}O_6N_8$, XLI, from Thermal Decomposition of [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9,[1H,6H]-tetraone, XXIII, at 350°C under Nitrogen (Run No. 2)

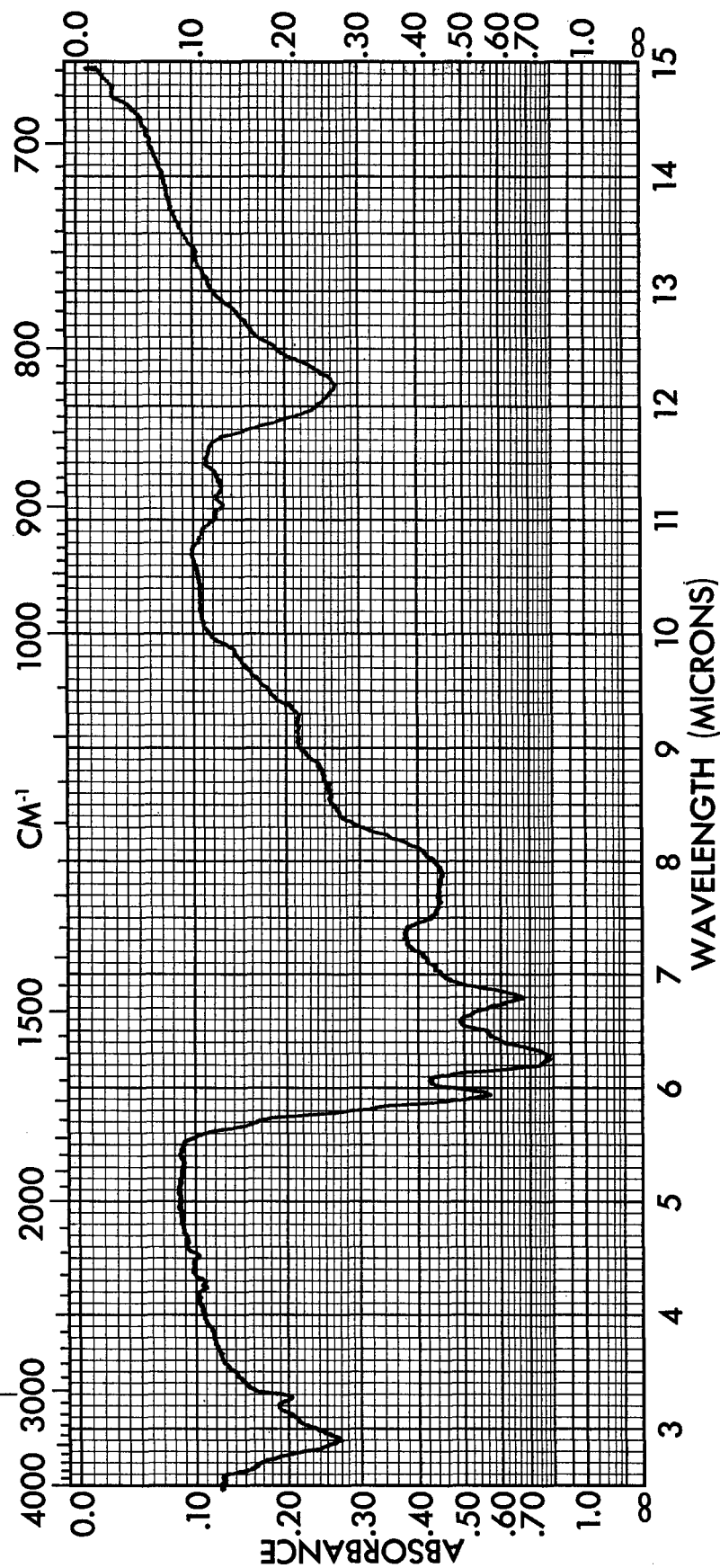


Figure 53. Infrared Spectrum of the Polymer $C_{28}H_{12}O_2N_4$, XLIV, from Thermal Decomposition of 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX, at 350°C under Nitrogen

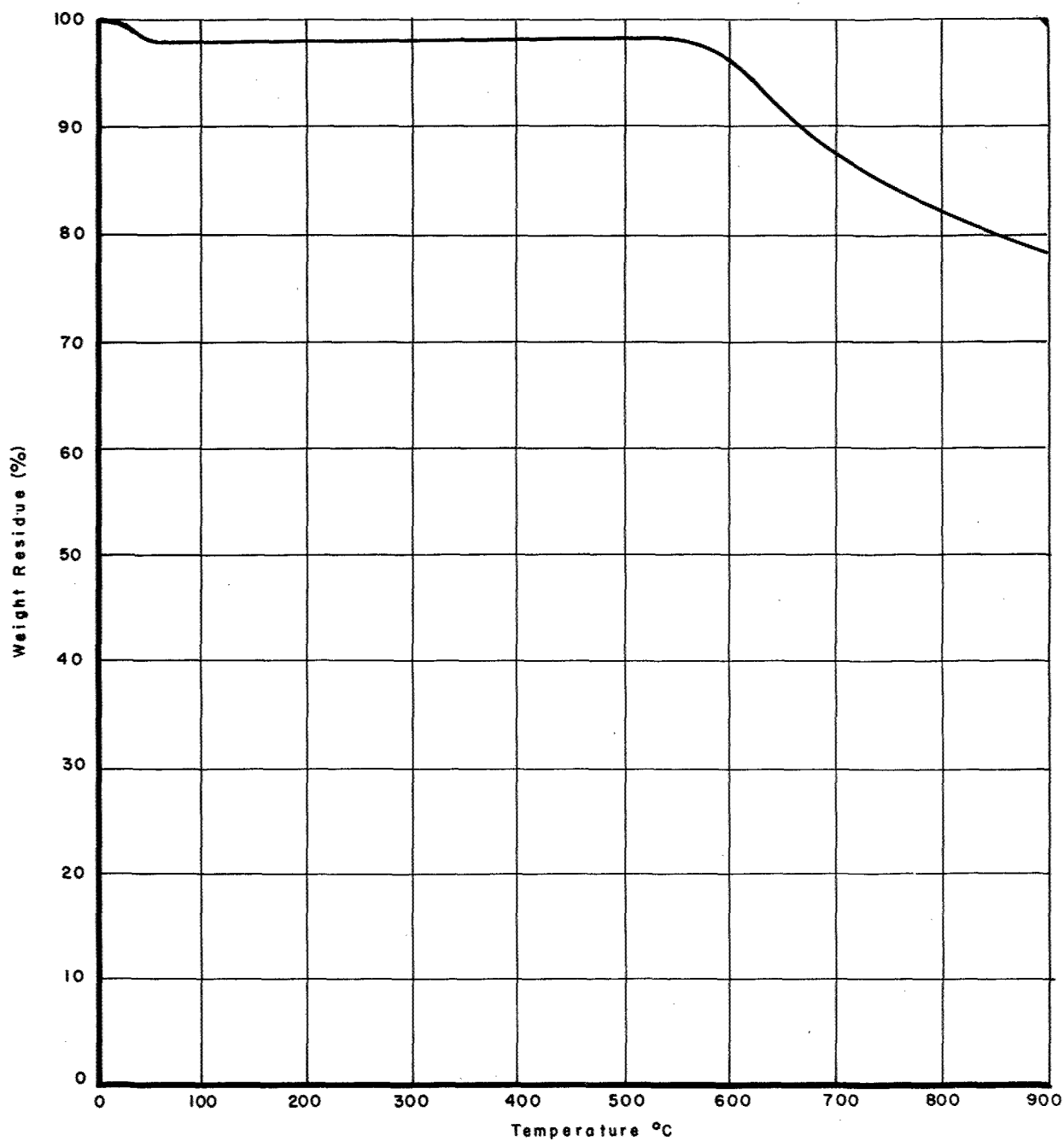


Figure 54. TGA Curve of the Polymer $C_{28}H_{12}O_2N_4$, XLIV, from Thermal Decomposition of 6,6'-bis-([2H],3,1-benzoxazine-2,4,[1H]-dione), XXIX, at 350°C under Nitrogen

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A new compound [2H, 7H], 3, 1, 8, 6-benzobisoxazine-2, 4, 7, 9, [1H, 6H]-tetraone was prepared by reaction of phosgene with 2, 5-diaminoterephthalic acid.

The thermal decomposition of [2H], 3, 1-benzoxazine-2, 4, [1H]-dione was studied as a model reaction. The reaction involves initial loss of carbon dioxide at 360°C and the formation of trimeric and tetrameric cyclic aryl amides, followed by dehydration to highly condensed structures.

[2H, 7H], 3, 1, 8, 6-benzobisoxazine-2, 4, 7, 9[1H, 6H] tetraone and 6,6'-bis-[2H], 3, 1-benzoxazine-2, 4, [1H]-dione each were decomposed thermally under similar conditions. The resulting products were highly condensed cross-linked polymers of high thermal stability.

14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	1. [2H,7H],3,1,8,6-benzobisoxazine-2,4,7,9, [1H,6H]-tetraone, Preparation of and Thermal Decomposition of						
	2. [2H],3,1-benzoxazine-2,4,[1H]-dione, Thermal Decomposition of						
	3. 6,6'-bis-[2H],3,1-benzoxazine-2,4[1H]-dione, Thermal Decomposition of						
	4. Cyclic Aromatic Polyamides						
	5. 10H, 21H-dibenzo-[3,4; 7,8][1,5]-diazocino- [2,1-b; 6,5-b']-diquinazoline-10, 21-dione						
	6. Poly-(5,6,11,12-tetrahydro-6,12-dioxodibenzo- [b,f][1,2,5]-diazocine-2,8-diyl)						